Technical Memorandum on the Derivation of Sediment Preliminary Remediation Goal (PRG) for the Ashland Lakefront Site

INTRODUCTION

The United States Environmental Agency (USEPA) and State of Wisconsin, Department of Natural Resources (DNR) have received and reviewed the second revised Remedial Investigation Report (RI Report) for the Ashland/Northern States Power Lakefront Superfund Site (Site) submitted by Northern States Power Company, a Wisconsin Corporation, a wholly owned subsidiary of Xcel Energy, Inc. (NSPW), pursuant to the Administrative Order of Consent (AOC) (V-W-04-C-764); between NSPW and the USEPA. The RI Report included a Baseline Ecological Risk Assessment (BERA) Report and a Remedial Action Objectives (RAO) Technical Memorandum, which proposes a sediment preliminary remediation goal (PRG) based on the conclusions of the BERA. For the reasons discussed in this Technical Memorandum and pursuant to Section X, (EPA Approval of Plans and Other Submissions), Subparagraph 21(c), of the AOC, USEPA hereby is modifying the RAO Technical Memorandum by incorporating the PRG contained herein. NSPW has 21 days to incorporate the PRG contained herein and resubmit the RAO Technical Memorandum based on EPA's modifications.

Previous BERAs were prepared for the Site by SEH under contract with DNR. SEH completed a BERA of the contaminated sediments adjacent to Kreher Park in 1998 (SEH, 1998). A supplemental BERA was performed in 2001 (SEH 2002), during which additional sediment toxicity testing was conducted to provide information describing the likelihood, nature, and severity of adverse effects to ecological receptors resulting from their exposure to contaminants at the Site. The NSPW iteration of the BERA was conducted to fill data gaps delineated through a data gap analysis of the earlier BERAs as requested by Xcel, and supplements the two other BERAs that have been conducted for this Site. The lack of data (i.e., data gap) in the 3 mg/kg to 300 mg/kg total polycyclic aromatic hydrocarbon (PAH) range of concentrations was to be filled during the NSPW iteration. After reviewing the NSPW BERA (revision 02), the USEPA has concluded that much of the past data collected during the 1998 and 2002 iterations of the BERA were not used to derive the conclusions presented in the NSPW BERA, which was required by the AOC.

This Technical Memorandum looks at the all of the data collected over the three iterations of sediment investigations, and following the sediment quality "triad" approach derives a range of concentrations of PAHs that would be expected to affect the benthic macroinvertebrate community. In addition, this Technical Memorandum draws upon the considerable body of information on PAH toxicity to benthic organisms to supplement the site data. From this range of contaminant concentrations and the expected effects to the benthic communities, USEPA proposes a preliminary remediation goal (PRG) for the sediment portion of the site that will be included in the RAO Technical Memorandum.

This Technical Memorandum does not constitute WDNR's and USEPA's complete comments to the submitted BERA (revision 02), but rather a streamlined approach to arriving at a PRG in order to keep the RI/FS process moving forward. The USEPA's comments to the BERA will be forwarded in a separate letter. These comments will be based on the NSPW's approved Work Plan and the USEPA letter dated September 1, 2006, commenting on the first BERA submittal, as well as subsequent meetings and response letter.

Following the sediment quality triad approach, the subsequent subsections describe the three measures of exposure used to evaluate sediment toxicity:

1) Evaluation of sediment chemistry;
2) Evaluation of site-specific toxicity tests; and
3) Evaluation of site-specific community studies.

Next, a range of PRGs is evaluated with the overall goal being protection of the survival, growth, and reproduction of benthic invertebrate communities. The PRGs produced in this document were derived from data collected through all iterations of sediment investigation at the Site and is based on USEPA review of all data collected. From these PRGs, a single PRG is proposed which will be used by NSPW to complete the Feasibility Study pursuant to the AOC.

1. Sediment Contaminant Chemistry

The sediment investigation conducted at the Site in 1996, and several subsequent investigations, identified the presence of extensive contamination, extending out to 700 feet offshore. Contaminants identified in the sediments include non-aqueous phase tars and oils, PAHs, petroleum volatile organic compounds, heterocyclic aromatic hydrocarbons, phenolic compounds and heavy metals.

The Supplemental BERA report (SEH, 2002) provided a summary of the various contaminants identified and a range of responses associated with the various levels of contamination. Ecological impacts were identified as likely being associated with a variety of the contaminants present. However, the BERA focused on PAHs since they appear to be present in the highest concentrations, are co-located with other contaminants, and appear to demonstrate a response effect.

The 2005 study conducted by URS on behalf of NSPW was intended to supplement the SEH 2002 study by addressing uncertainties related to the range of total PAH (TPAH) concentrations. Sediment Quality Triad (SQT) stations were to be distributed across TPAH concentrations from approximately 2,000 ug/kg to 300,000 ug/kg TPAH (dry weight, dwt), to represent a range of concentrations that encompasses those concentrations where potential ecological effects were likely to be found. At each SQT location, chemical analysis appears to have been conducted for a composite grab sample; each of five replicate samples used for the benthic community study; and a laboratory homogenized sample utilized for bioassay toxicity tests. Particle size analysis was also conducted for the replicate samples.

Attachment 1 provides a summary of the TPAH, total organic carbon (TOC), and particle size data reported for the 2005 samples. The new data does supplement the 2002 BERA study in that it provides data on the variation at replicates sampling locations. Additionally, the supplemental data for new reference sites provides further information related to background levels.

At many of the sampling sites, calculation of the mean, median, and standard deviation reveals large variation among TPAH concentration in the replicates. At SQT1, SQT7, and SQT8, the standard deviation exceeded the mean and the median. It is apparent the TPAH concentration data are widely dispersed at these locations and that the mean is a poor representation of the data set. For example, at SQT1 the TPAH concentrations among replicates varied over two orders of magnitude, ranging from 12,994 mg/kg to 1,162,300 mg/kg. This variation in data reinforces the need to apply a conservative approach in the interpretation of sediment chemistry results to minimize the potential for underestimating effects at each SQT location.

Background reference site locations are useful for establishing a potential lower boundary for the sediment PRGs, as it is not typically reasonable to set cleanup objectives lower than background concentrations. As shown on Attachment 1, the TPAH concentrations at the reference sand (composite grab samples, homogenized samples and replicate results) were very similar to the 1998 reference sand site location, where the TPAH concentration was 500 ug/kg dwt @ 0.46% OC).

2. <u>Site-Specific Sediment Toxicity Bioassays</u>

Sediment toxicity bioassays conducted in 1998 and 2001 were summarized in the SEH (2002) BERA Supplement. Toxicity tests were conducted for a wide range of TPAH exposures ranging from 424 ug/kg to 836,300 ug/kg TPAH (dwt). Results of the tests indicated that acute (lethal) impacts were always demonstrated above the WDNR draft TPAH probable effect concentration (PEC) of 22,800 ug/kg (at 1% TOC). At concentrations below the WDNR draft TPAH threshold effect concentration (TEC) of 1,610 ug/kg (at 1% TOC), acute impacts were demonstrated only when toxicity tests were conducted with UV exposures. At concentrations between the TEC and PEC, a variety of lethal and sublethal impacts were observed.

The 2005 bioassay study conducted by URS was intended to supplement the SEH studies by addressing uncertainties related to the range of TPAH contaminant concentrations and by including several toxicity tests for both sand and wood substrates.

Attachment 2 includes a "stoplight diagram" that summarize the 1998, 2002, and recent URS study results for the sediment bioassay toxicity tests for sandy sediments. The diagram does not include the results of bioassays conducted with woody sediment, elutriate or UV light exposures. Discussions with Xcel/URS have indicated their interest in establishing RAOs based on dry weight normalized PAH concentrations in sandy sediments and applying that same value as the RAO for woody sediments.

USEPA evaluation of the toxicity tests conducted with UV light exposures are provided in Attachment 3. The evaluation provides an analysis of expected photo-activated lethal effects expected to be associated with various TPAH concentrations (normalized to 0.41 % OC in sand) and UV exposures related to variable depths within the water column. The evaluation presents survival response curves illustrating sediment toxicity with and without UV exposures. A survival response curve integrating both the URS 2006 results and SEH 2001 results illustrates that a close relationship exists between the test results.

3. Site-Specific Sediment Macroinvertebrate Surveys

The benthic macroinvertebrate community investigation presented in the 1998 BERA (SEH, 1998) indicated that community degradation correlated to sediment TPAH contamination. Subsequent statistical evaluations of the 1998 data by both the WDNR and Dames & Moore in 1999 (excerpts included in Attachment 4 indicated strong correlation between sediment TPAH concentrations and several benthic community metrics, although it was acknowledged the data set was small and the range of contaminant concentrations was limited. The 2005 study conducted by URS was intended, in part, to supplement the 1998 study to address uncertainties related to sample size and range of contaminant concentrations.

According to the EPA's *Guidance Manual to Support the Assessment of Contaminated Sediments in Freshwater Ecosystems – Volume III – Interpretation of the Results of Sediment Quality Investigations* (EPA-905-BO2-001C, December 2002), "the information on benthic community structure can not be used alone to evaluate the cause of any impacts observed. While such communities certainly respond to chemical contamination in the sediment they are also affected by a wide range of physical factors that are not directly related to sediment quality (e.g., low dissolved oxygen levels, grain size differences, nutritional quality of substrates and water depth). In addition, benthic community composition exhibits significant spatial, short term temporal, and seasonal variability." Thus, if a study encounters a large degree of variability such that discriminatory power is greatly decreased, then the strength of the benthic community study as a line of evidence is decreased commensurately. It appears that there was tremendous variability and resultant uncertainty associated with both the site samples and reference samples collected in the URS 2005 benthic macroinvertebrate community investigation.

Issues associated with the variability and the uncertainty of the 2005 sampling sites used in the statistical evaluation of benthic community impacts include but are not limited to:

- The range of TPAH concentrations for SQT1 replicate samples overlapped the range of TPAH concentrations of most other SQT replicate samples;

- The standard deviation of the dataset exceeds the mean values for TPAH concentrations for replicate samples SQT1, SQT7, SQT8 and reference wood site SQT11;

- The standard deviation of the dataset exceeds the mean value for TOC concentration for reference wood site SQT9;

- The percentage of fine sands is higher in 80% of the reference samples than in 100% of site samples;

- The percentage of fines + fine sands is higher in 80% of the reference samples than in 75% of the site samples;

- The reference sand sites SQT10 and SQT12 exhibited "a strong odor of decaying organic matter" and "elevated levels of ammonia";

- The reference sand sites SQT10 and SQT12 exhibited <50% survival for *Hyalella azteca* 28 day sediment exposure toxicity test;

- The reference wood site SQT11 had no survival in several replicates of the *Lumbriculus* bioaccumulation study;

- The reference sand sites SQT13 and SQT 14 were collected in Fall 2005 versus Spring 2005, more than 3 months after the initial sample collection. Use of this data is questionable for comparison of population metrics due to expected seasonal variation in larval and emergent species; and

- Only three site locations appear to be "sand" sites, and none of the reference sand sites appear to be appropriate. Thus, the sample size for sand sediments does not appear meet the power requirements outlined in the RI/FS workplan.

The statistical analysis presented in the BERA appears to have included benthic community data without "clear and transparent" discussion of how the aforementioned issues were addressed. Input of questionable information into a statistical model produces questionable results and yields low power. If the benthic community study has low power, then it is prone to underestimating effects and is in fact a weak line of evidence rather than a strong one.

It is also noted that the 2005 study neglected to evaluate metrics that appeared to have statistical significance in the 1998 study including midge/oligochaete ratios and midge taxa richness (although this metric was listed in the RI/FS workplan).

Unfortunately, the 2005 benthic community study analysis, as presented in the BERA documentation, provides little value in supplementing the 1998 study and it does not lend value to the current discussion of PRGs.

4. Sediment Quality Triad Integration to Develop a Preliminary Remediation Goal

The accumulated data for sediment chemistry, bioassay toxicity tests, and benthic macroinvertebrate community surveys at this site continue to indicate that it is reasonable to conclude ecological impact is highly likely and contaminant-induced degradation of sediment-dwelling organisms is evident. Several approaches have been evaluated to calculate a site-specific PRG for the sediment TPAH concentrations. The alternate PRGs are presented below in order of ascending concentrations.

1) The 2002 Supplemental ERA calculated a PRG of **274 ug TPAH/kg dwt** for sandy sediments based on the mean of the no observed effect concentration (NOEC) and the lowest observed effect concentration (LOEC) related to the sediment elutriate dilution series for fathead minnows. USEPA is uncertain if the sediment elutriate dilution series may have overestimated aquatic exposures and effects.

2) The toxicity test conducted in 1998 with the contaminated sand sample (616 ug TPAH/g OC or 1,539 ug TPAH/kg dry weight (dwt) @ 0.25% TOC) resulted in sublethal effects for the midge toxicity test. Lethal effects were also documented with this sample with fathead sediment elutriate exposures, lethal effects with *Daphnia magna* sediment elutriate exposures (coupled with UV), and lethal effects associated with the *Lumbriculus variegates* sediment exposures (coupled with UV). Using the 1998 contaminated sand sample as the "low observed effects" sample and 1998 reference sand sample (109 ug TPAH/g OC or 500 ug/kg @ 0.46% TOC) as the "no observed effects" sample yields a mean value of **362 ug TPAH/g OC** (1,020 ug/kg @ 0.36% TOC).

3) Attachment 5 includes a discussion by David Mount (USEPA) related to PAH toxicity thresholds for the site sediments. The document discusses the various impacts that may be associated with a range of sediment TPAH concentrations. The lowest value discussed is **1,340 ug TPAH/g OC** (5,570 ug TPAH/kg dwt @ 0.415% TOC). The discussion of UV toxicity included in Attachment 3 appears to indicate this value would also provide protection from photoactivated toxicity effects for 80% of *Hyallela azteca* in water depths ranging from 2 to 8 feet (with no debris cover). It is noted that this concentration may not address potential sublethal effects.

4) The discussion by Dave Mount (Attachment 5) also indicates that the remediation goal of **5,310 ug TPAH/g OC** (22,000 ug TPAH/kg dwt @ 0.415% TOC) recommended by URS in the 2007 BERA is likely to result in substantial acute toxicity to *Hyalella*. *Lumbriculus*. and *Chironomus* species.

5) Based on a variety of data sources, the EC20 for midge is expected to lie within a range of 1340 to 3930 ug PAH/g OC (Attachment 5). At an OC of 0.415%, this corresponds to 5.6 to 16.3 ug PAH/g dwt. Use of the EC20 is consistent with the

data quality objective (DQO) for sediment bioassays which states: "If control survival is = 80%, and the difference between Site survival or growth and reference station survival or growth is = 20% (statistically significant difference at a= 0.1) it is indicative of unacceptable risks" (25 January 2005 BERA, Appendix G, Table 4. Data Quality Objectives for 28 day *Hyalella azteca* (Amphipod) with and without UV Light and 20-day *Chironomus dilutus* (formerly *C. tentans) (Midge) Sediment* Bioassay). The proposed PRG for sediment is 2,295 ug PAH/g OC (9.5 ug PAH/g dwt at 0.415% OC), which is the geometric mean of the above range.

SUMMARY AND CONCLUSIONS

The sediment chemistry and toxicity data presented in the NSPW BERA support the 1998 and 2002 SEH BERA data. The "high weight of evidence" that NSPW attempts to place on the benthic macroinvertebrate community study is not supported by USEPA guidance or the community study data and has little support from the 1998 BERA study. With the variability and uncertainty outlined above, the statistical analysis of the community data is questionable; as such, it was not used to derive the proposed PRG.

The NSPW sediment chemistry data supports earlier chemistry data. The NSPW toxicity testing supports the 1998 and 2001 SEH data sets and supports the PRGs previously proposed in these documents. The UV results from the 2005 study also support the earlier work. In addition, the bioassay data is in agreement with the body of data available in the literature on concentrations of TPAHs that produce toxic effects on benthic communities. Thus, both the chemistry data and the toxicity data are used to support the determination of a PRG for the Site.

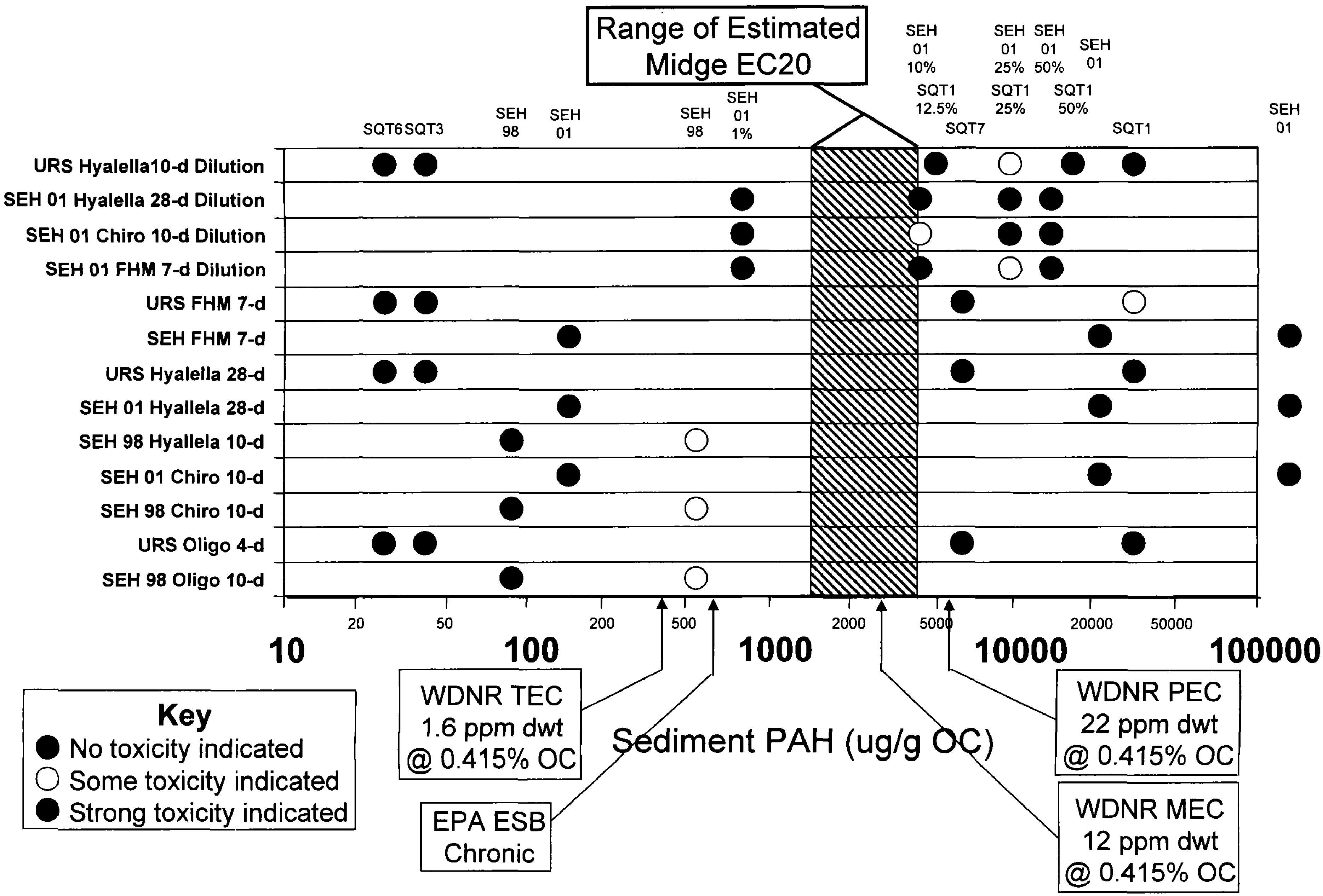
In conclusion, the proposed PRG **[2,295 ug PAH/g OC (9.5 ug PAH/g dwt at 0.415% OC)]** is based on a best professional evaluation of sediment chemistry, bioassay, and benthic community study data collected by SEH and NSPW and conclusions reached by NSPW. This PRG does not include the added effects of UV and is based on a water depth of 6 feet or more. If the final depth of sediments will be less than 6 feet, the PRG for any active remedial intervention will be adjusted downward as based upon UV extinction coefficients measured in Site waters. The adjusted PRGs (assuming no debris cover) are provided in Table 1 of Attachment 3.

Since the RI/FS Work Plan was approved by USEPA, a number of correspondence and meetings have taken place in an attempt to come to a mutually agreed upon PRG for sediment contamination at the Site. A number of differences in application of the data have continued to interfere with this pursuit. In order to keep on schedule for completion of the Feasibility Study, the USEPA has produced this Technical Memorandum. Pursuant to the AOC, NSPW will complete the ordered Feasibility Study using the PRG contained in this Technical Memorandum.

List of Attachments

1	Sediment Chemistry Data from URS 2005 BERA
2a	Summary of Results for Sandy Sediments
2b	Summary of Results for Woody Sediments
3	20 January 2007 Memorandum on "Analysis of Photoactivation Issue Relative to Ashland BERA"
4	Excerpts from WDNR and Dames & Moore (1999)
5	March 26, 2007 Memorandum on "Discussion of PAH Toxicity Thresholds for Ashland Site Sediments"

Figure 1 -- Summary of Toxicity Data for Sandy Sediments



Attachment 1
Sediment Chemistry Data from URS 2005 BERA

					PARTICLE SIZE ANALYSIS OF SEDIMENTS							
Sample ID#, Date of Collection	**TPAH (dw ug/kg)**	**TOC (dw mg/kg)**	**TOC (%)**	**TPAH NOC (ug/g OC)**	**% Solids**	**Non-Soil Mass %**	**Gravel Size %**	**Coarse Sand Size %**	**Medium Sand Size %**	**Fine Sand Size %**	**Silt & Clay Fines % Size (<P200)**	**% S&C Fines and Fine Sand**
SQT 9, Reference woody site, June 2005												
SQT 9 Mean of Replicates	426	20,808	2.1%	35	55	11	0.0	0.3	21	75	4	80
Standard Deviation +/-	*-*	*23,103*	*2.3%*	*17*	*9*	*8*	*0.0*	*0.2*	*3*	*7*	*4*	*4*
Median	*426*	*10,500*	*1.1%*	*41*	*58*	*7*	*0.0*	*0.3*	*21*	*73*	*4*	*80*
SQT 9 Composite Grab	334	32,000	3.2%	10								
SQT Tox Test Homogenized Sample	83	58,000	5.8%	1								
SQT 10, Reference sandy site, June 2005												
SQT 10 Mean of Replicates	426	4,320	0.4%	140	74	1	0.0	0.2	10	87	3	90
Standard Deviation +/-	*-*	*3,905*	*0.4%*	*58*	*3*	*1*	*0.0*	*0.1*	*4*	*4*	*3*	*4*
Median	*426*	*2,600*	*0.3%*	*164*	*72*	*1*	*0.0*	*0.2*	*9*	*89*	*2*	*91*
SQT 10 Composite Grab (TPAH avg with Dup)	230	860	0.1%	268								
SQT Tox Test Homogenized Sample	26	1,300	0.1%	20								
SQT 11, Reference woody site, June 2005												
SQT 11 Mean of Replicates	9,856	502,600	50.3%	20	29	131	0.0	0.0	25	48	29	76
Standard Deviation +/-	*12,611*	*80,996*	*8.1%*	*25*	*4*	*50*	*0.0*	*0.0*	*7*	*23*	*19*	*8*
Median	*4,260*	*499,000*	*49.9%*	*10*	*29*	*129*	*0.0*	*0.0*	*22*	*37*	*31*	*78*
SQT 11 Composite Grab	740	78,000	7.8%	9								
SQT Tox Test Homogenized Sample	3,798	280,000	28.0%	14								
SQT 12, Reference sandy site, June 2005												
SQT 12 Mean of Replicates	1,106	869	0.1%	1,264	74	0	0.2	0.0	1.3	96	3	99
Standard Deviation +/-	*570*	*55*	*0.0%*	*605*	*1*	*0*	*0.2*	*0.0*	*0.3*	*2*	*1*	*0*
Median	*852*	*872*	*0.1%*	*990*	*74*	*-*	*0.0*	*0.0*	*1.2*	*96*	*3*	*99*
SQT 12 Composite Grab (TPAH avg with dup)	435	407	0.0%	1,069								
SQT Tox Test Homogenized Sample	8	320	0.0%	26								
SQT 13, Reference sandy site, September 2005												
SQT 13 Mean of Replicates	426	2,742	0.3%	157	69	-	0.0	0.0	0.8	94	5	99
Standard Deviation +/-	*-*	*268*	*0.0%*	*15*	*1*	*-*	*0.0*	*0.0*	*0.1*	*1*	*1*	*0*
Median	*426*	*2,750*	*0.3%*	*155*	*70*		*0.0*	*0.0*	*0.8*	*94*	*5*	*99*
SQT 13 Composite Grab (TPAH avg with dup)	224	2,460	0.2%	91								
SQT Tox Test Homogenized Sample	NO DATA PROVIDED											
SQT 14, Reference sandy site, September 2005												
SQT 14 Mean of Replicates	426	3,866	0.4%	113	73	-	0.6	0.4	12	80	7	87
Standard Deviation +/-	*-*	*665*	*0.1%*	*18*	*3*	*-*	*0.5*	*0.1*	*2*	*2*	*1*	*2*
Median	*426*	*3,820*	*0.4%*	*120*	*74*		*0.4*	*0.5*	*13*	*80*	*7*	*87*
SQT 14 Composite Grab (TPAH avg with dup)	67	2,800	0.3%	24								
SQT Tox Test Homogenized Sample	NO DATA PROVIDED											

Attachment 1
Sediment Chemistry Data from URS 2005 BERA

Sample ID#, Date of Collection	TPAH (dw ug/kg)	TOC (dw mg/kg)	TOC (%)	TPAH NOC (ug/g OC)	*PARTICLE SIZE ANALYSIS OF SEDIMENTS* % Solids	Non-Soil Mass %	Gravel Size %	Coarse Sand Size %	Medium Sand Size %	Fine Sand Size %	Silt & Clay Fines % Size (<P200)	% S&C Fines and Fine Sand
SQT 1, sandy site, June 2005												
SQT1 Mean of Replicates	442,595	6,196	0.6%	57,118	79	2	0.0	0.5	32	60	8	68
Standard Deviation +/-	*487,715*	*3,524*	*0.4%*	*42,721*	*2*	*4*	*0.1*	*0.3*	*4*	*5*	*5*	*3*
Median	*260,275*	*4,950*	*0.5%*	*70,155*	*79*	*1*	*0.0*	*0.6*	*32*	*60*	*9*	*68*
SQT 1 Composite Grab (TPAH avg with dup)	376,815	3,175	0.3%	118,682								
SQT Tox Test Homogenized Sample	166,940	4,600	0.5%	36,291								
SQT 2, woody site, June 2005												
SQT 2 Mean of Replicates	3,545	427,400	42.7%	9	37	82	0.0	0.0	32	45	24	69
Standard Deviation +/-	*1,314*	*139,292*	*13.9%*	*3*	*5*	*30*	*0.0*	*0.1*	*13*	*12*	*22*	*11*
Median	*3,283*	*385,000*	*38.5%*	*8*	*37*	*79*	*0.0*	*0.0*	*33*	*48*	*19*	*67*
SQT 2 Composite Grab	4,815	100,000	10.0%	48								
SQT Tox Test Homogenized Sample	3,195	420,000	42.0%	8								
SQT 3, woody site, June 2005												
SQT 3 Mean of Replicates	21,989	294,400	29.4%	68	35	52	0.0	0.0	9	53	38	91
Standard Deviation +/-	*14,228*	*140,190*	*14.0%*	*19*	*10*	*32*	*0.0*	*0.0*	*4*	*16*	*17*	*4*
Median	*25,235*	*364,000*	*36.4%*	*69*	*34*	*41*	*0.0*	*0.0*	*8*	*47*	*48*	*92*
SQT 3 Composite Grab (TPAH avg with dup)	*21,270*	*136,500*	*13.7%*	*156*								
SQT Tox Test Homogenized Sample	*17,060*	*400,000*	*40.0%*	*43*								
SQT 4, woody site, June 2005												
SQT 4 Mean of Replicates	20,302	420,201	42.0%	56	29	161	0.0	0.0	22	50	28	78
Standard Deviation +/-	*6,214*	*120,013*	*12.0%*	*36*	*2*	*58*	*0.0*	*0.0*	*8*	*13*	*18*	*8*
Median	*19,390*	*461,000*	*46.1%*	*42*	*30*	*146*	*0.0*	*0.0*	*24*	*52*	*24*	*76*
SQT 4 Composite Grab	26,942	160,000	16.0%	168								
SQT Tox Test Homogenized Sample	14,098	420,000	42.0%	34								
SQT 5, woody site, June 2005												
SQT 5 Mean of Replicates	57,462	348,600	34.9%	172	31	75	0.0	0.0	23	46	31	77
Standard Deviation +/-	*17,101*	*135,253*	*13.5%*	*34*	*3*	*12*	*0.0*	*0.0*	*8*	*6*	*13*	*8*
Median	*54,500*	*363,000*	*36.3%*	*157*	*31*	*74*	*0.0*	*0.0*	*23*	*46*	*35*	*77*
SQT 5 Composite Grab (TPAH avg with dup)	84,003	265,500	26.6%	316								
SQT Tox Test Homogenized Sample	31,250	250,000	25.0%	125								
SQT 6, sandy site, June 2005												
SQT 6 Mean of Replicates	4,155	79,060	7.9%	52	36	8	0.0	0.0	4	22	74	96
Standard Deviation +/-	*1,879*	*15,550*	*1.6%*	*15*	*2*	*5*	*0.0*	*0.0*	*1*	*6*	*6*	*1*
Median	*3,505*	*82,900*	*8.3%*	*48*	*36*	*7*	*0.0*	*0.0*	*4*	*20*	*76*	*96*
SQT 6 Composite Grab	9,038	14,000	1.4%	646								
SQT Tox Test Homogenized Sample	2,297	95,000	9.5%	24								
SQT 7, sandy site, June 2005												
SQT 7 Mean of Replicates	21,209	2,352	0.2%	16,148	78	2	0.2	0.7	36	59	4	63
Standard Deviation +/-	*25,828*	*1,078*	*0.1%*	*26,426*	*3*	*2*	*0.4*	*0.4*	*1*	*2*	*2*	*1*
Median	*13,720*	*2,190*	*0.2%*	*4,314*	*78*	*1*	*0.0*	*0.6*	*36*	*59*	*4*	*63*
SQT 7 Composite Grab (TPAH avg with dup)	14,058	3,100	0.3%	4,535								
SQT Tox Test Homog Sample (avg TPAH with dup)	23,096	3,500	0.4%	6,599								
SQT 8, woody site, June 2005												
SQT 8 Mean of Replicates	116,331	290,840	29.1%	288	36	70	14.4	0.3	24	48	14	62
Standard Deviation +/-	*161,989*	*179,095*	*17.9%*	*344*	*12*	*71*	*13.3*	*0.5*	*7*	*6*	*11*	*14*
Median	*86,630*	*309,000*	*30.9%*	*182*	*33*	*52*	*21.9*	*0.2*	*23*	*51*	*16*	*63*
SQT 8 Composite Grab	124,238	42,000	4.2%	2,958								
SQT Tox Test Homog Sample (TPAH Avg with Dup)	59,137	385,000	38.5%	154								

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OFFICE OF
RESEARCH AND DEVELOPMENT

April 5, 2007

SUBJECT: Analysis of photoactivation issue relative to Ashland BERA

FROM: David R. Mount, Research Aquatic Biologist

TO: Scott Hansen, RPM Ashland Superfund Site

The following text describes my assessment of the predicted effects of combined UV and PAH exposure at the Ashland site based on the available experimental data. A draft of this memo was reviewed by Dr. Russell Erickson; his comments were incorporated and he is in agreement with the analysis.

For short term exposure, response to UV/PAH exposure has been shown to be proportional to the product of the PAH exposure (often expressed in terms of body burden) and the UV exposure. In the case of sediment exposure without measured body burdens, the sediment PAH concentration (OC normalized) should be a reasonable surrogate for PAH dose if one assumes that the organisms came to a steady state body burden relatively quickly. The uncertainty here is on the side of leniency (i.e. the opposite of environmentally conservative) as it would underestimate effects if steady state was not achieved. Under the steady state assumption, the expression of exposure as a product of sediment PAH concentration and UV exposure should be an appropriate way to compare results among experiments.

Figures 1 and 2 show the exposure-response relationships for the URS (2006) and SEH (2001) exposures of *Hyalella* to dilutions of a sandy PAH contaminated sediment from the site, with and without UV light. The PAH concentration for the 50% dilution in the SEH study has been adjusted as suggested previously by URS. These experiments show that the addition of UV light to sediment exposure consistently increases toxicity. In the URS study, the increase in toxicity from a 24-hour average UV of 28.3 $\mu W/cm^2$ (a 16-h photoperiod averaged over 24 hours) was about 2.1 fold, with the LC50 decreasing from 12750 μg PAH/g OC to 6050 μg PAH/g OC. In the SEH test, the average UV exposure was slightly higher (24-h average of 34.5 $\mu W/cm^2$) and the increase in toxicity was about 2.7 fold, with the LC50 decreasing from 14418 to 5351 μg PAH/g OC. Taking into account the slightly higher UV in the SEH tests, these results are remarkably close.

One difference between the URS and SEH tests is test duration – the URS test was a 10-d test, while the SEH test was a 28-d test. Because the UV dose is cumulative and therefore increases with time of exposure, one might expect that a longer exposure would show comparable effects at a lower PAH concentration. However, despite the difference in duration, the LC50 values expressed on the basis of sediment PAHs were remarkably close. One explanation for this similarity might be that the duration of the SEH exposure was long enough for damage repair rates to become significant. The concept that the potency of UV/PAH exposure is a linear function of PAH * UV * time assumes that accumulated damage from UV/PAH exposure is repaired at a negligible rate, which appears to be true for shorter term exposures. However, it is reasonable to expect that for less severe exposures, which create damage at a slower rate over longer periods, repair rates will become significant. Thus, it may be that LC50 concentrations become asymptotic at longer exposure periods such as 10-28 days.

A second explanation is that the PAH exposure in the URS and SEH tests differed in a way not reflected by the reported PAH concentrations in the sediment. The evidence for this explanation is that the SEH 28-d *Hyalella* test without supplemental UV showed lower sensitivity to PAHs (28-d LC50 14400 μg PAH/g OC) than did the 10-d test without UV conducted by URS (10-d LC50 12700 μg PAH/g OC). Based on literature data (e.g., Schuler et al. 2004; ES&T 38:6247), one would expect the 28-d LC50 in the absence of UV light to be about half of the 10-d LC50.

For purposes of this analysis the former explanation, that damage repair becomes significant in longer term exposures, was used. While a more lenient (as opposed to environmentally conservative) assumption, it is not excessively so, and is very consistent with what one would expect from the underlying biology. Under this assumption, one can compare the two test responses by plotting them on the same axis using average daily UV/PAH exposure ([μW-h UV/cm^2] * [μg PAH/g OC]). Doing so is strongly suggestive of a single exposure response curve with an LC50 of 4.2 [W-h UV/cm^2] * [μg PAH/g OC] and an LC20 of 2.947 [μW-h UV/cm^2] * [μg PAH/g OC] (Figure 5).

The two UV experiments discussed above were both conducted to simulate UV intensity at moderate depth, circa 8 feet. However, UV penetration is highly depth dependent, so much greater UV intensity can be expected at shallower depths. EPA suggested to URS/Xcel on multiple occasions that additional UV exposures should be conducted at higher UV intensities in order to quantify the expected response at shallower depths. However, URS/Xcel declined to follow EPA's suggestion, so the BERA is left to extrapolate results representing moderate depths to responses that would be expected at shallower depths.

To do this, the extinction curve determined from UV measurements at the site was used to estimate the degree of light penetration at various. The extinction equation was:

% of surface UV at x cm depth = 10^(-0.0064*x+1.9769)

Based on previous calculations, the 24-h average UVA irradiance at the water's surface in June was estimated at 977 μW/cm^2. The expected 24-h dose expected at any depth equals the percentage UV penetration to that depth multiplied by the surface UVA multiplied by 24 hours. This can be divided by 10^6 to convert μW to W. If one divides the LC20 (from the PAH/UV response regression described above) by the depth-specific 24-h UV dose just described, the result is the sediment PAH concentration expected to result in 20% lethality to *Hyalella* at that depth. Table 1 shows the results of these calculations.

A final issue relates to the degree to which overlying debris might provide partial shading to benthic organisms living at the site. All of the exposures discussed thus far have had no shading provided aside from the test sediment itself. To explore the shading issue, URS conducted an additional series of treatments in which leaf plugs were added to the test chambers to provide shade like might be expected from a sediment surface with overlying debris. The results of this exposure series, compared to the response obtained without UV, and with UV but without shading, is shown in Figure 6. These data indicate an intermediate response by organisms exposed in the presence of leaf plugs. The presumption is that the decreased sensitivity of *Hyalella* to UV/PAH in the presence of leaf plugs is associated with decreased UV exposure, although no measurements were made to determine if the presence of leaf plugs might have decreased bioavailability and/or accumulation of sediment PAHs. Previous analyses conducted by Dr. Russell Erickson of EPA/ORD-Duluth (provided to Xcel as part of initial EPA comments on the draft BERA) empirically estimated the amount of shading provided by the presence of leaf plugs, based on the differential responses among treatments with no UV, and UV with and without leaf plugs. The estimate was that the presence of overlying debris (leaf plugs) reduced UV exposure by 40%. This value can be used to estimate the expected response of *Hyalella* in the presence of overlying debris, by recalculating the depth-specific PAH LC20 concentrations assuming 40% less UV exposure. These "with debris" values are shown along with the "no debris" LC20 values in Table 1. Selection of thresholds to apply at the site depends on the degree to which overlying debris is expected (before or after remedial action) and how the shading effect of the debris layer would relate to that used in the laboratory experiments. in this range would depend on the degree to which overlying debris is available at the site, both before and after any remedial action. Table 1 also shows these LC20 values adjusted to a dry weight basis, assuming an organic carbon content of 0.415%, the average of the OC content in SQT1 and SQT7.

The extrapolation to UV exposures expected in areas shallower than 8 ft presumes that the increase in UV exposure of benthic organisms will be proportional to the increase in incident UV at the sediment surface, and that the UV alone will not cause adverse effects. Because Xcel/URS declined to conduct testing at UV intensities higher than those expected in roughly 8 feet of water, any non-linearities that might occur in the real world cannot be estimated, and direct proportionality is the only reasonable assumption (i.e., if one doubles the UV, the PAH concentration corresponding to the LC20 will be cut in half). There has been some preliminary experimental work conducted at EPA's Duluth laboratory using PAH-spiked sediments and simultaneous UV exposure. This work is neither complete nor published. However, it suggests that *Hyalella* can withstand continuous UVA exposure to at least 290 $\mu W/cm^2$ (highest exposure tested) in the presence of West Bearskin sediment (no overlying debris) without apparent adverse effect, and *Chironomus dilutus* and *Lumbriculus variegatus* withstood continuous UVA exposure of about 770 $\mu W/cm^2$ (highest exposure tested) in sediment without overlying debris. While these are preliminary data, they suggest that UVA exposure alone would not prevent colonization of sediments with higher UVA exposure, although whether there is an upper limit was not determined in these experiments.

The discussion above relied exclusively on data from UV/PAH exposures with *Hyalella azteca* as the basis for estimating effect thresholds. However, several other experiments involving UV/PAH exposure were conducted during the course of site investigations. The relationship between these other studies and the analysis above is discussed in the following paragraphs.

URS (2006) also conducted exposures of larval fathead minnows to both site sediments and simultaneous UV exposure. UV exposures used in these experiments were higher than those in the *Hyalella* exposures, intended to represent UV intensity in about 4 feet of water rather than the 8 feet assumed for the *Hyalella* exposures. In terms of sediment PAH concentration associated with effects, the fathead minnows appeared comparably sensitive as *Hyalella*. Survival in SQT7 was 38% percent, with a PAH concentration of 6084 ug/g OC. This 38% survival is about half that observed in the reference treatments, so one can view 6084 as an approximate LC50 for fathead minnows at the associated UV exposure. As described above, the LC50s for *Hyallela* were 6050 and 5351 ug/g OC. In absolute terms, this implies that fathead minnows were less sensitive than *Hyalella* to UV/PAH exposure because UV exposure was higher in the fathead minnow test. Regardless, the comparison of the fathead minnow and *Hyalella* tests suggest that fathead minnows would likely be protected by thresholds calculated based on the whole sediment exposures with *Hyalella* as shown in Table 1.

Additional experiments (SEH 1998) were conducted using organisms that were exposed UV light in clean water, after exposure to contaminated sediments without simultaneous UV. These exposures were relatively short (hours) and involved relatively high UV irradiance (circa 500 $\mu W/cm^2$). While these experiments definitely demonstrate that organisms accumulated contaminants from the sediments that could be photo-activated by UV exposure, the intense UV exposure and the absence of the shading effect of sediment (as would be available in nature) make it difficult to interpret these exposures relative to the effects one would expect under field conditions.

Finally, some UV/PAH experiments were conducted using sediment elutriates. Elutriate experiments can be challenging to interpret if actual exposures are not measured. Because experimental data are available for organisms simultaneously exposed to UV and PAH in bedded sediments, it does not appear necessary to apply data from elutriate experiments to risks associated with organisms exposed to bedded sediments. Elutriate experiments may have greater applicability to a resuspension event, though the absence of measured PAH concentrations in the elutriates make it difficult to directly relate the PAH exposure occurring in the elutriate experiments to concentrations of PAHs that might occur in the water column at the site during a resuspension event. In addition, hydrodynamic events of sufficient magnitude to resuspend substantial amounts of sediment would likely also affect UV penetration into the water column. Additional analysis and/or data collection would be necessary to comprehensively evaluate the potential for photo-activated toxicity under a resuspension scenario.

Table 1. Sediment PAH concentrations estimated to cause 20% lethality of *Hyalella azteca* in 10 days of exposure with and without overlying debris.

Water Depth (cm)	% of Surface Irradiance at Depth	24-h Average Irradiance ($\mu W/cm^2$)	PAH at LC20 (ug/g OC)		PAH at LC20 (ug/g dwt @ 0.415% OC))	
			No Debris	With Debris	No Debris	With Debris
5	88.1	860.6	143	238	0.59	0.99
10	81.8	799.5	154	256	0.64	1.06
25	65.6	640.9	192	319	0.80	1.33
50	45.4	443.4	277	462	1.15	1.92
100	21.7	212.2	579	964	2.40	4.00
150	10.4	101.6	1210	2020	5.02	8.36
200	4.98	48.6	2530	4210	10.5	17.5
232	3.11	30.3	4050	6750	16.8	28.0
250	2.38	23.3	5280	8800	21.9	36.5
300	1.14	11.1	11000	18400	45.8	76.3

Figure 1 URS 2006 Sandy Dilution

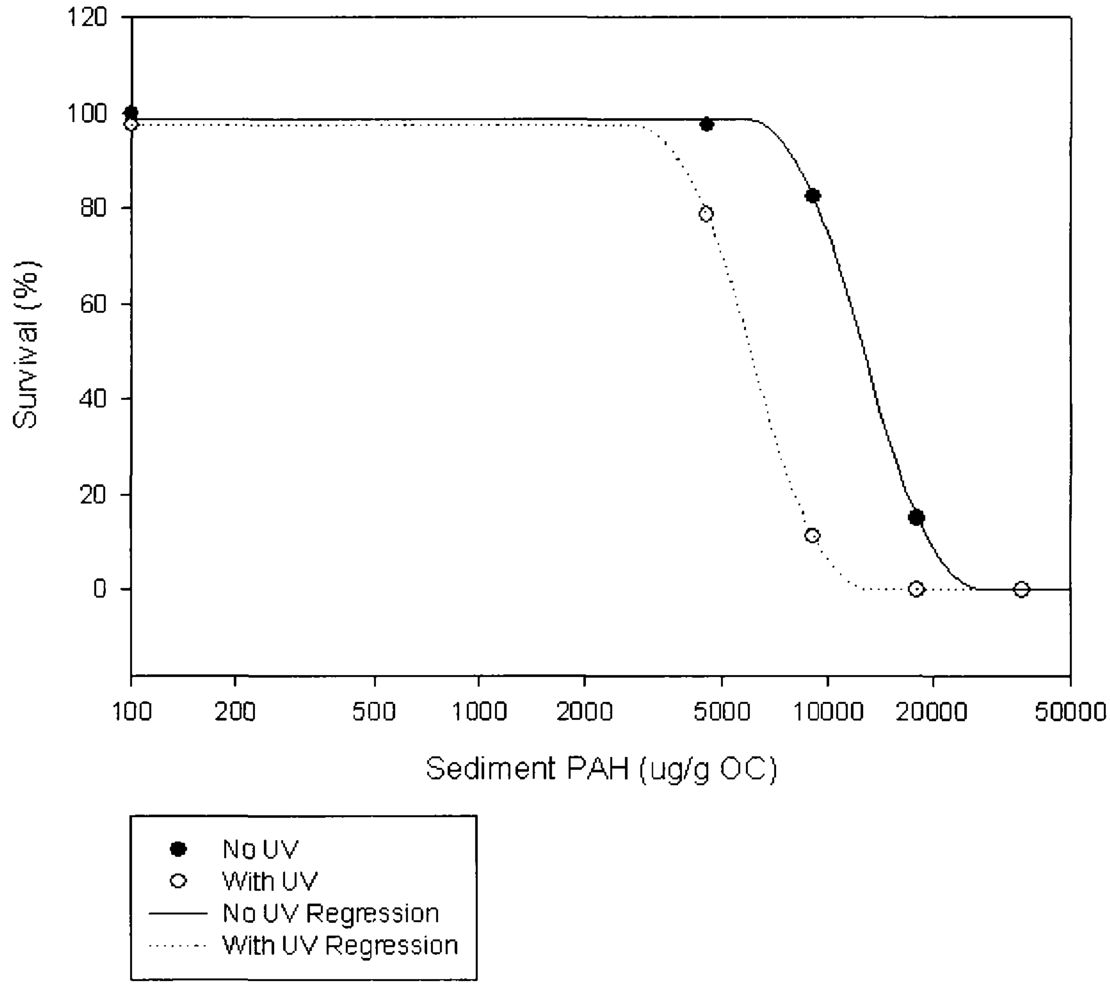


Figure 2 SEH 2001 Sandy Dilution

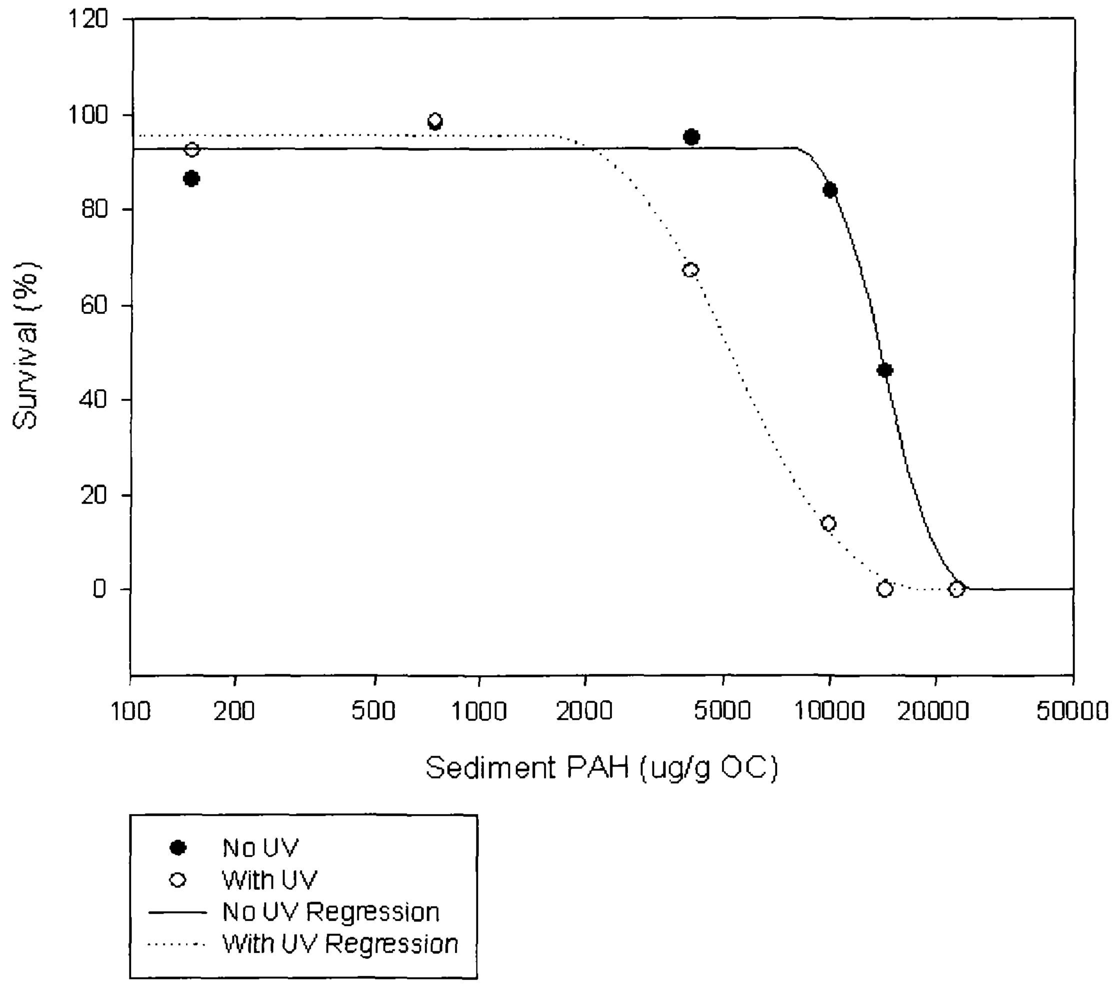


Figure 3 URS 2006 Sandy Dilution with UV

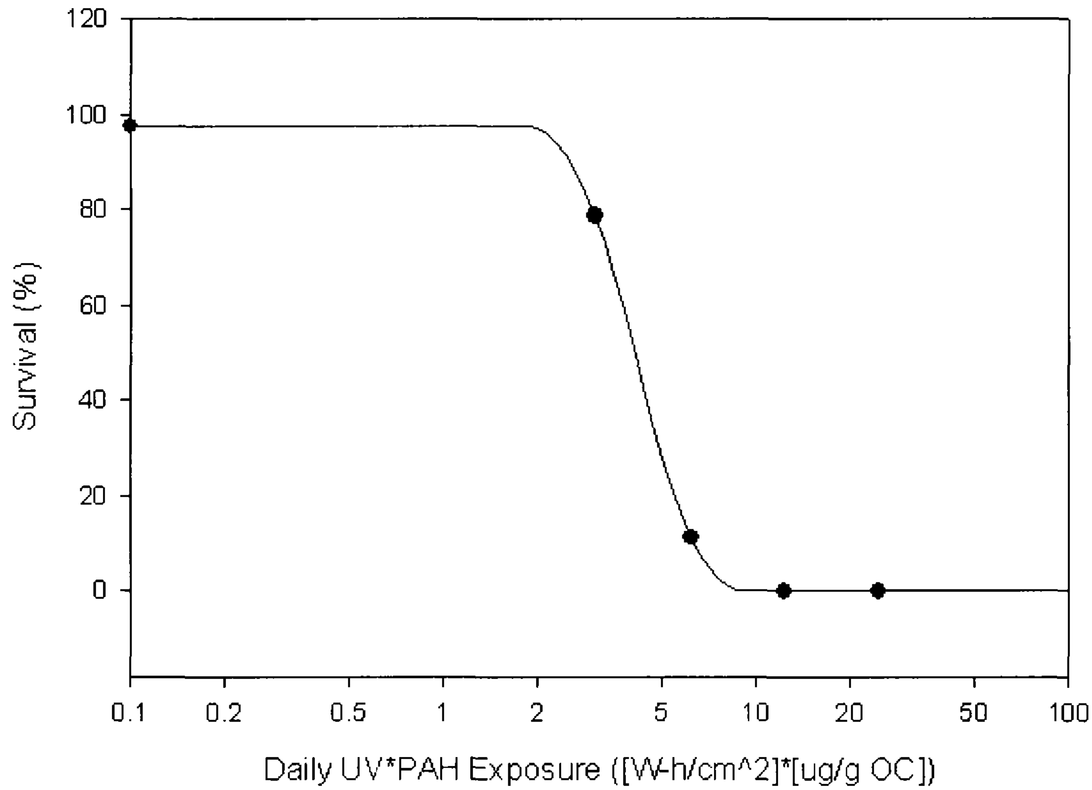


Figure 4 SEH 2001 Sandy Dilution with UV

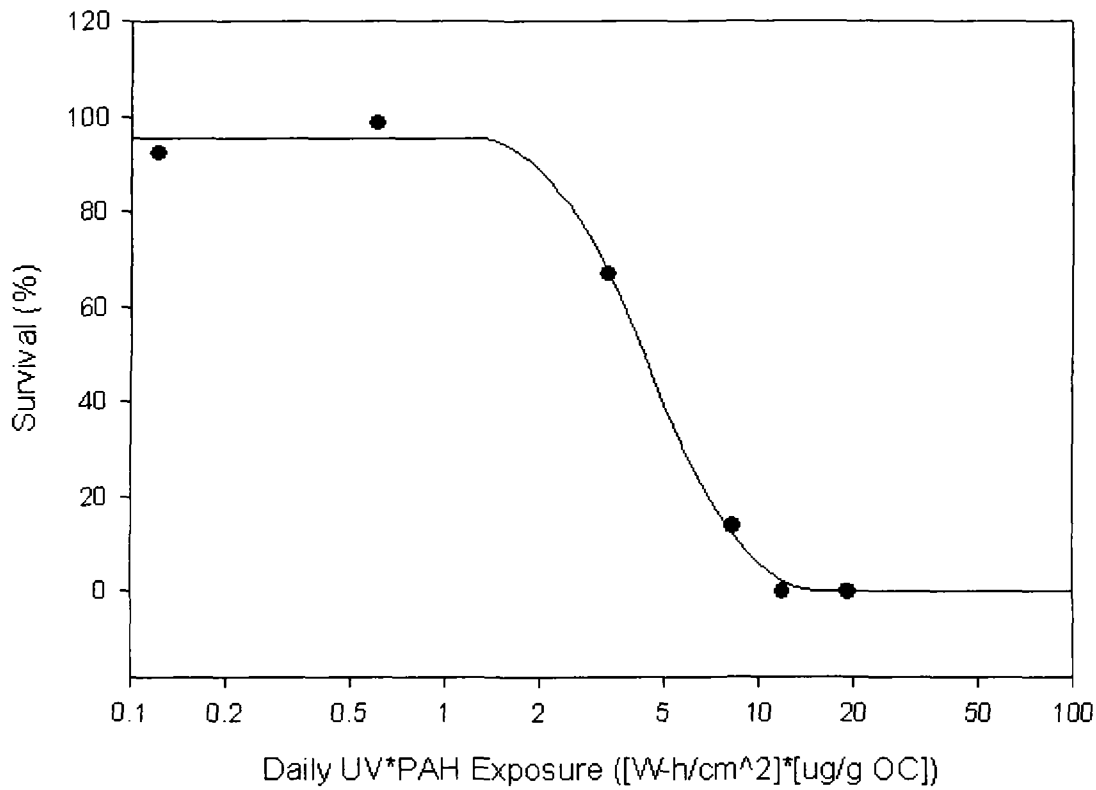


Figure 5 Combined Sandy Dilution with UV

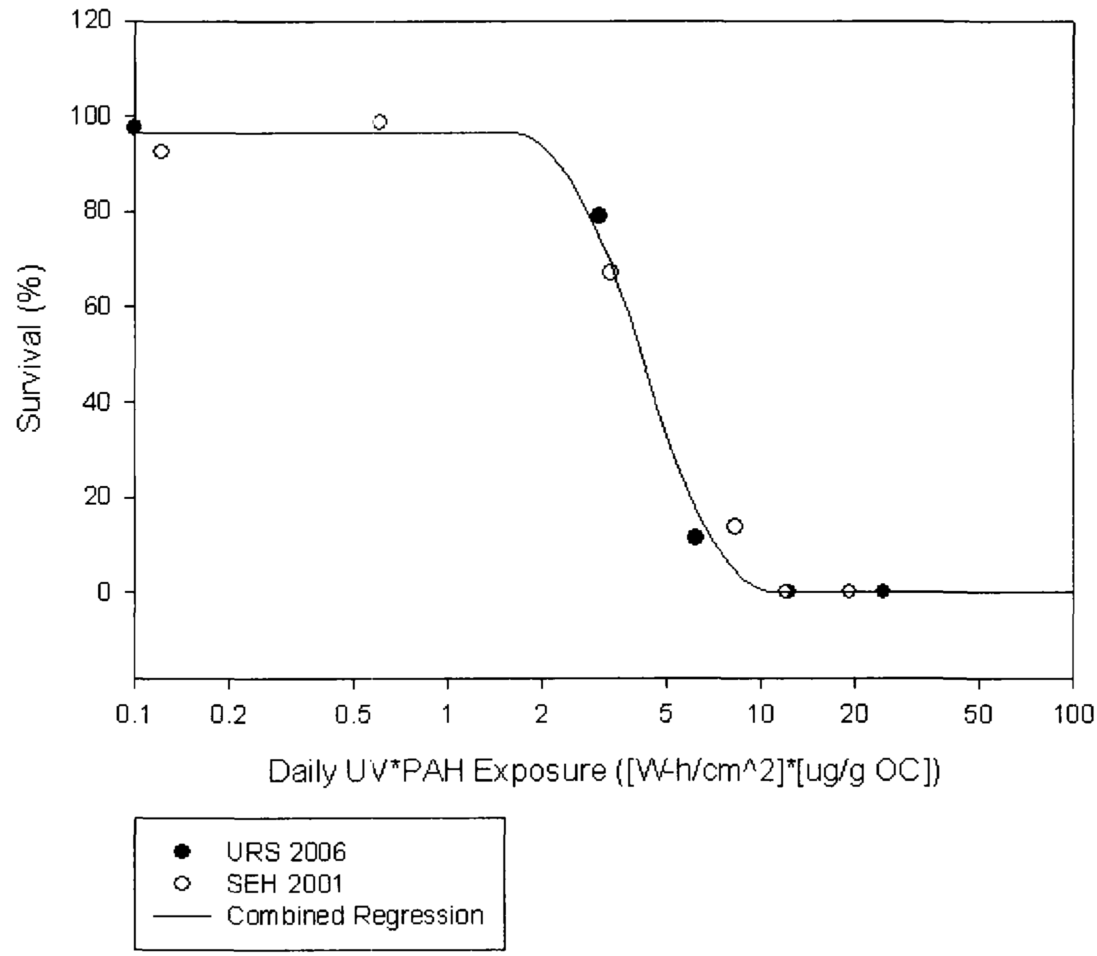
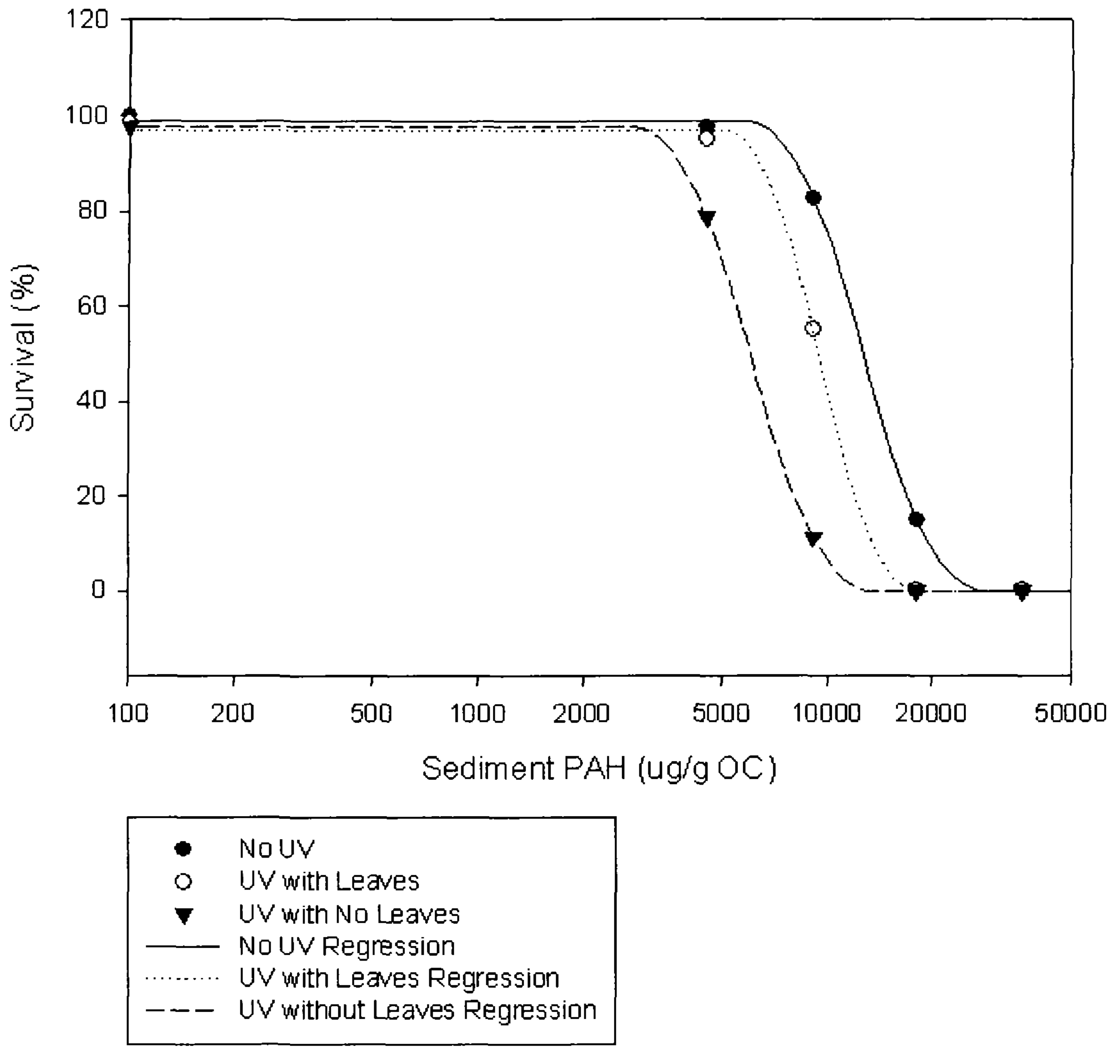


Figure 6 URS 2006 Sandy Dilution



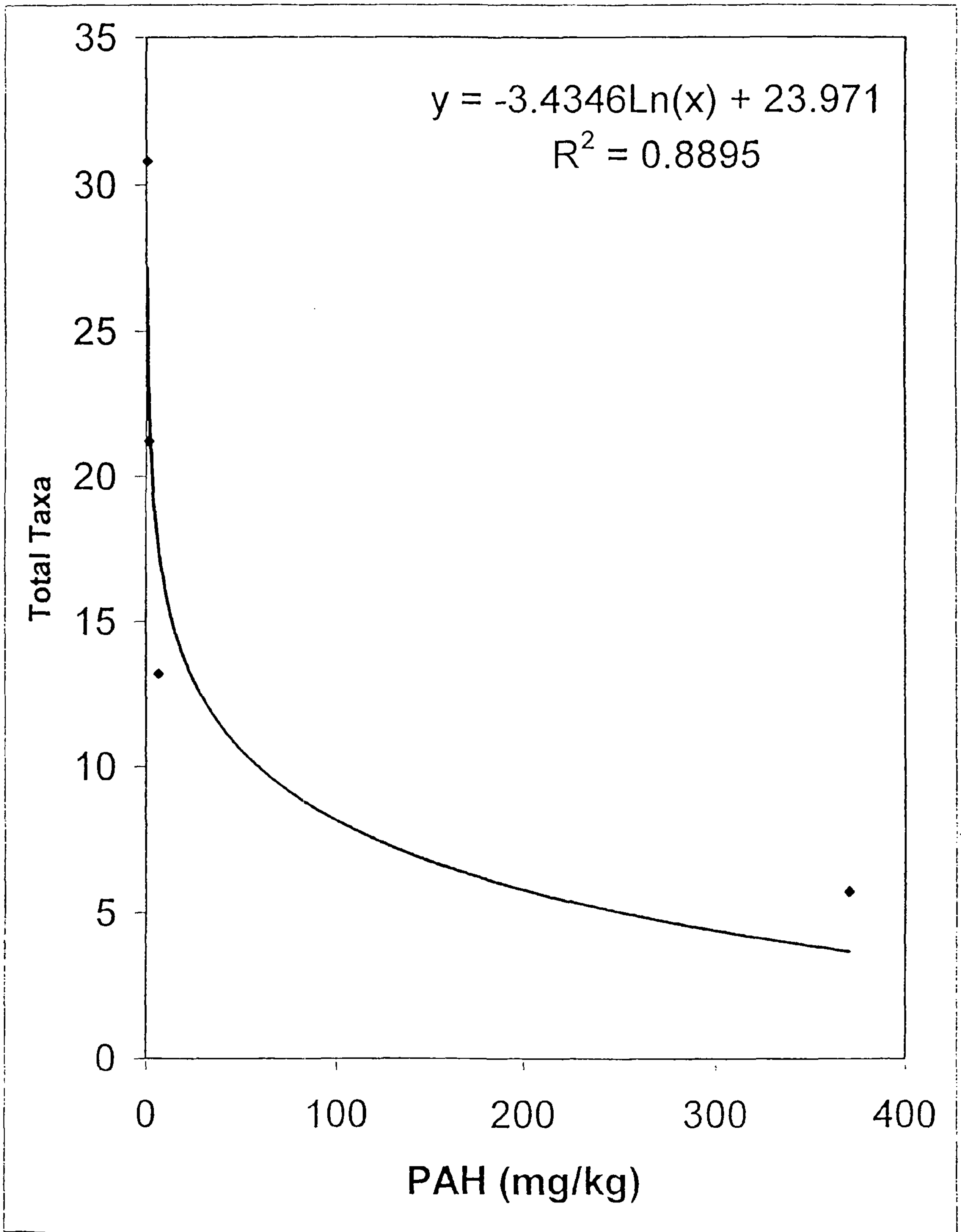
A statistical analyses was done on the paired sampling results from each substrate to determine if the results were significantly different. Separate t-tests (alpha less than or equal to 0.05) were run to compare the raw data from the two sand sites and the two wood sites. Data were transformed when necessary to achieve normality and equal variance by using natural log or natural log (x + 1) (if zero values were present in the data). Normality was tested using the Kolmogorov-Smirnov Test (with Lilliefors' correction), while equal variance was tested using the Levene Medial Test. If normality or equal variance could not be achieved, a Mann-Whitney Rank Sum Test was used. All tests were done using SigmaStat (Jandel Scientific, San Rafael, CA.). The paired results that were shown to be statistically different and the level of significance are shown in the table below. The eight indices that are significantly different in the table below are the same eight identified in the table above through qualitative means that were related to probable impacts from the coal tar contamination.. The statistical analyses confirms the conclusions reached through the qualitative evaluation of the data.

Indices	Comparison of RW:CW Index Means Level of Significance		Comparison of RS:CS Index Means Level of Significance	
Total Taxa Richness	Significant	$p = 0.019$	Significant	$p = 0.004$
Midge Taxa Richness	Significant	$p = 0.002$	Significant	$p = 0.007$
Total Abundance (m2)	Not significantly different	$p = 0.838$	Significant	$p < 0.001$
Midge Abundance (m2)	Significant	$p = 0.002$	Significant	$p < 0.001$
Oligochaete Abundance (m2)	Not significantly different due to high variability at contaminated site	$p = 0.294$	Significant	$p < 0.001$

The end results of the above comparisons is the identification of four additional indices from the four identified by D & M which show probable impacts when the reference site results are compared to the contaminated site results on a qualitative and quantitative statistical basis.. The above results also generally coincide with the SEH ERA qualitative analysis of the macroinvertebrate data as shown in Table 15 of the ERA.

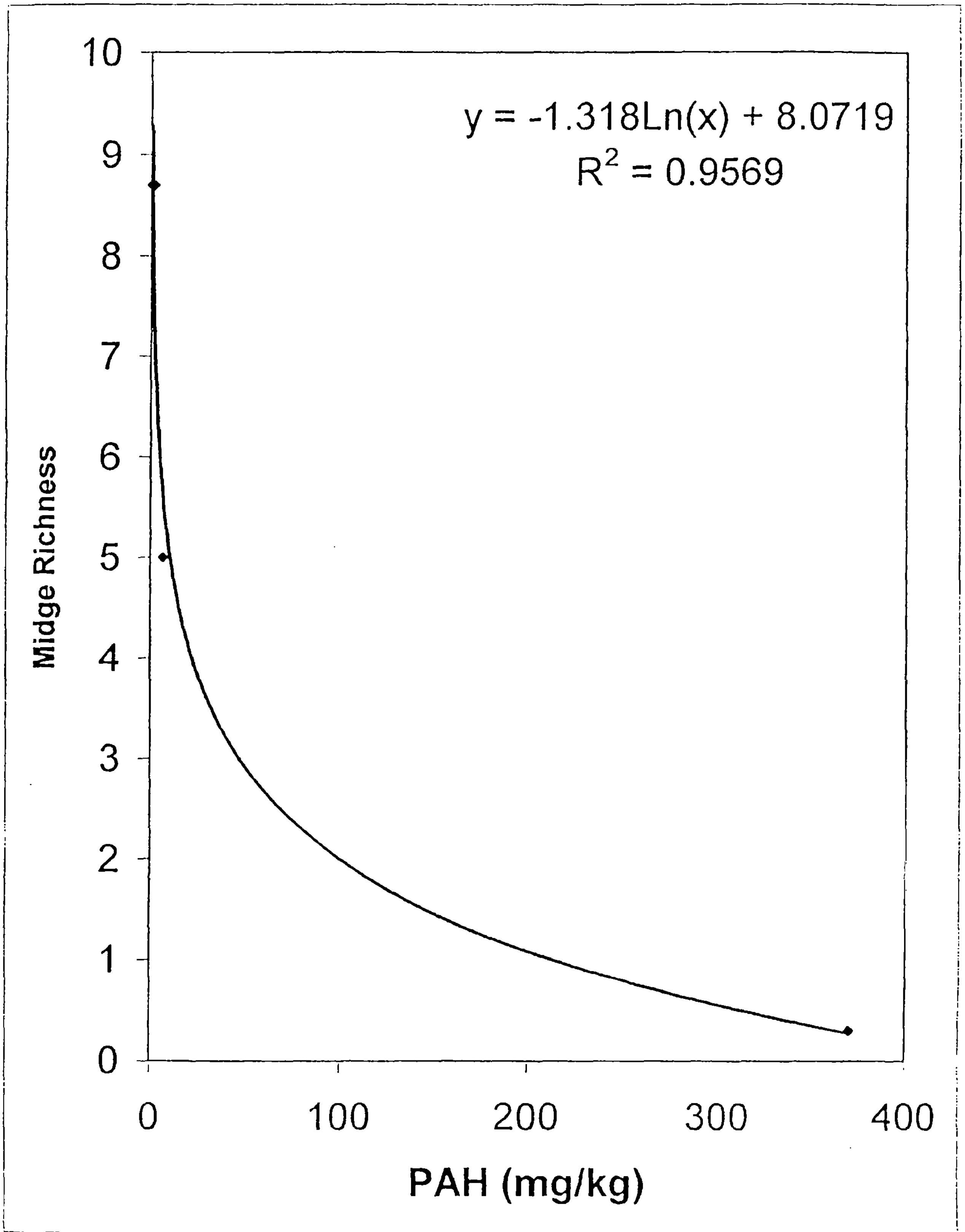
Source: WDNR (Tom Janisch) 1999 comments to D&M 1999 ERA

FIGURE 10



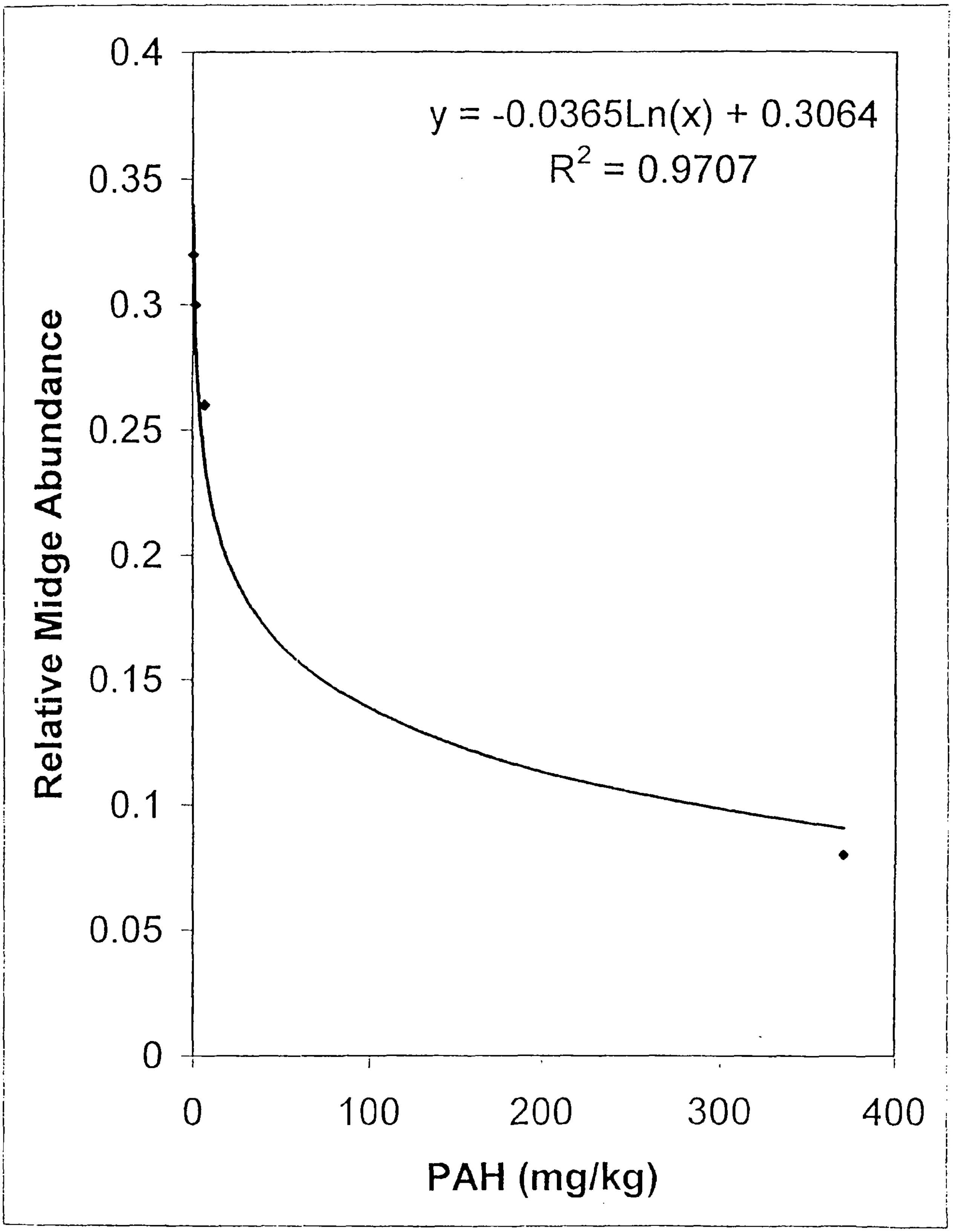
Source D&M March 1, 1999 ERA

FIGURE 11



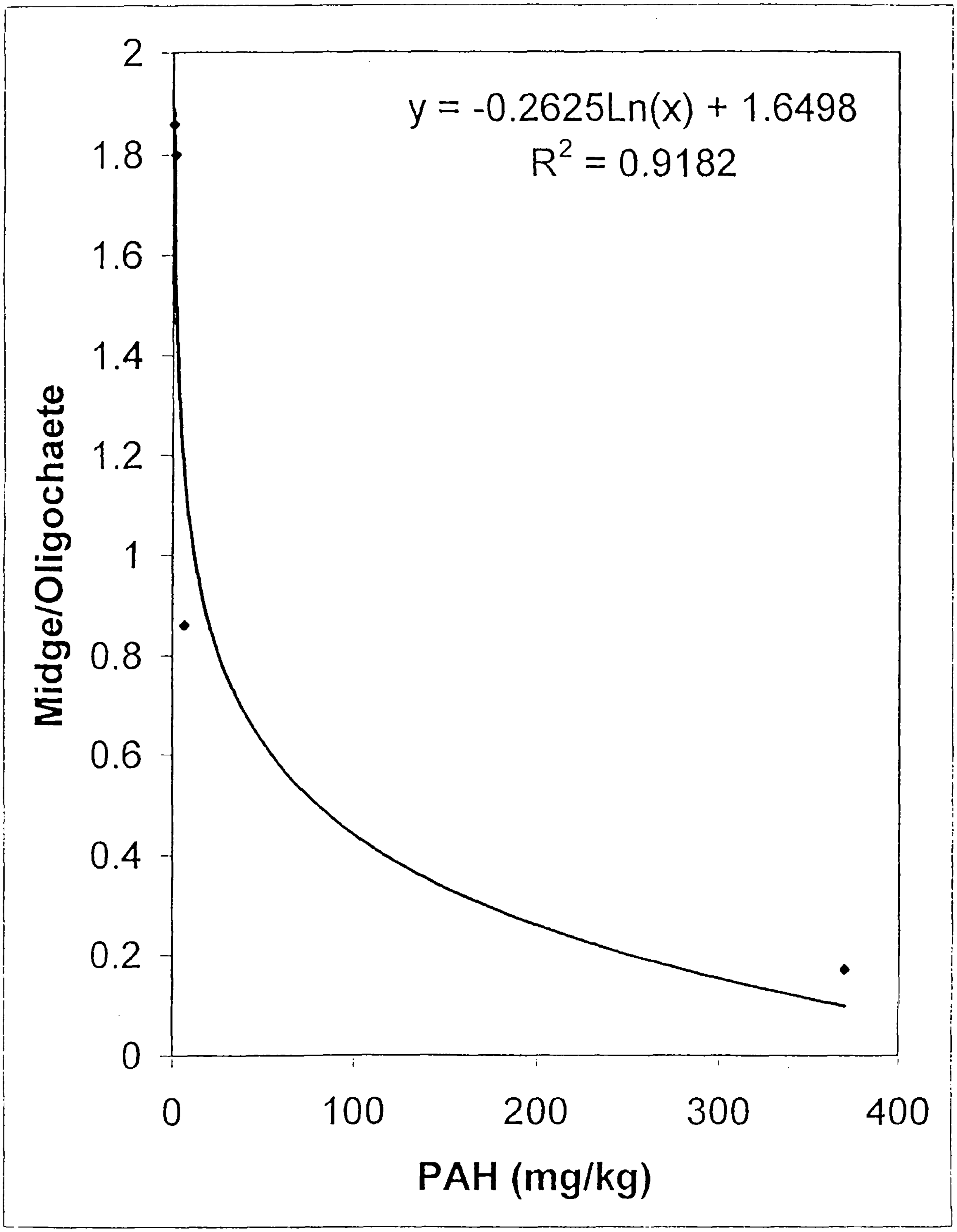
y = -1.318Ln(x) + 8.0719
R2 = 0.9569
Midge Richness
10
9
8
7
6
5
4
3
2
1
0
0
100
200
300
400
PAH (mg/kg)

FIGURE 15



y = -0.0365Ln(x) + 0.3064
R2 = 0.9707
Relative Midge Abundance
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
100
200
300
400
PAH (mg/kg)

FIGURE 16


y = -0.2625Ln(x) + 1.6498
R2 = 0.9182
Midge/Oligochaete
PAH (mg/kg)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0
100
200
300
400

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OFFICE OF
RESEARCH AND DEVELOPMENT

March 26, 2007

SUBJECT: Discussion of PAH toxicity thresholds for Ashland site sediments

FROM: David R. Mount, Research Aquatic Biologist

TO: Scott Hansen, RPM Ashland Superfund Site

I am writing to summarize my thoughts on establishing effect thresholds for PAH toxicity to benthic organisms from bedded sediments at the Ashland site. As you are aware from the recent string of written and telephone communications, the nature of the available data do not allow establishment of an effects threshold that is without uncertainty. Three major factors are responsible for this:

1) Not all studies targeting similar responses find the exact same exposure response profile;

2) Not all species tested have the same sensitivity;

3) While several studies have been completed, there remains a substantial gap in the toxicological information for a critical range of PAH concentrations, primarily 600 to 6000 μg/g organic carbon.

Xcel/URS have proposed a concentration of 53 ug total PAH/g[1] dwt as delineating sediments that have sufficient potential for adverse effect to require active remediation. From conversations with you, you have indicated that the remedial action objective (RAO) relative to protection of the benthic community should be a concentration expected to protect not just a single benthic organism, but the suite of benthic organisms evaluated. This is, of course, completely consistent with other regulatory approaches taken by the Agency; ecological protection is generally based on protecting most, if not all species, not just one. With this in mind, the RAO proposed by Xcel/URS fall short of your stated goals in two broad ways:

1) **An analysis of the available toxicity data, along with literature data, makes clear that toxicity due to the mixture of site PAHs can be expected well below 5300 μg/g OC, the value from which the RAO of 53 μg/g was derived.**

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[1]Unless otherwise noted, the term "total PAH" in this document refers to the sum of the PAH structures measured by URS in their analyses supporting the BERA. Note that a true measured of "total PAH" would include additional structures not quantified by URS in routine analyses.

2) **The 1% organic carbon content used by Xcel/URS to convert the purported effect "threshold" of 5300 μg/g OC to the RAO of 53 μg/g dwt is not reflective of the organic carbon content in the sediments which were the primary determinants of that threshold (0.37% and 0.46%). This has the effect of raising the proposed RAO (expressed on a dry weight basis) by a factor of 2.4-fold above the exposures actually shown to cause the effects Xcel/URS concedes are unacceptable.**

In the paragraphs that follow, I will discuss in detail why these two issues are critical, and how they can be more appropriately addressed. I will deal with the second issue first, as it is somewhat less complicated.

Translation Between Organic Carbon and Dry Weight Normalized Concentrations

The overwhelming evidence from the scientific literature shows clearly that partitioning to organic carbon (OC) controls the bioavailability, and therefore toxicity, of non-polar organic chemicals such as PAHs. For this reason, concentrations of PAHs in sediment are generally normalized on the basis of organic carbon for purposes of ecological risk assessment, as they are in the draft BERA. For this reasons, two sediments with the same dry weight (dwt) normalized PAH concentration may have pose greatly different ecological risks if their OC contents differ. However, there is often a preference on the part of remedial engineers and others to express remedial goals on a dwt basis rather than an OC basis. While this is contrary to toxicological theory, it is a practical reality, so a conversion is necessary.

This is a particularly important issue for the Ashland site, because the organic carbon contents of site sediments vary by more than a factor of 100-fold, from less that 0.4% to over 40%. This is further complicated by the belief that in sediments with relatively higher OC content, the OC is dominated by comparatively undegraded woody material, which can be suspected to have a lower affinity (i.e., lower partition coefficient) for PAHs than the more typical diagenic organic carbon likely to comprise the OC fraction in sandy, low OC sediments. If the partition coefficient for woody debris is in fact lower than that for diagenic carbon (and there is some evidence for this in the URS bioaccumulation studies and the SEH toxicity studies), then a different exposure/response relationship would be needed to determine the RAO for woody sediments. In discussions with Xcel/URS, it was proposed by Xcel/URS that a single, dwt-based RAO be developed based on responses in sandy sediment, and the same value would then be used for both sandy and woody sediments. Based on my review of the available data, I believe that establishing the RAO based on dwt-normalized concentrations in sandy sediments would in fact be protective of organisms in woody sediments if the same dwt-based RAO was applied.

Xcel/URS proposed an RAO of 53 μg total PAH/g dwt (total PAH being defined as the total of the PAH structures URS measured in their investigations), which was derived from a value of 5300 μg/g OC converted to a dwt basis assuming a OC content of 1%. The problem with this conversion is that the sediments that were primary drivers for the establishment of this threshold (SQT1 and SQT7) had organic carbon content well below 1% (0.46% and 0.37%, respectively). In fact, sediment SQT7, which was egregiously toxic to both *Hyalella* and *Lumbriculus*, had a dwt normalized PAH concentration of only 22.5 μg/g dwt. According to the RAO proposed by

Xcel/URS (53 µg/g dwt), SQT7 would not warrant active remediation, being less than half the RAO concentration, even though it was highly toxic to all species tested. Clearly, this is not consistent with a goal of protecting the suite of organisms evaluated in the BERA.

Because of this problem, the conversion of an OC-normalized threshold to a dwt-normalized RAO must consider the likely OC content to which the RAO will apply, not just a generic conversion assuming 1% organic carbon. Sampling by URS of sandy sediments both on and off site clearly indicate OC contents well below 1%. Later in this memo I will provide recommendations for dwt-normalized thresholds. For this purpose, I will use the mean of the OC measured in SQT1 and SQT7, which is 0.415%. Whether this is the exact value that should be used probably warrants further evaluation, though it is clear that something lower than 1% is necessary to accurately reflect the toxicity of sandy site sediments.

Summary: To protect benthos in sediment with the organic carbon content found in sandy site sediments collected and studied by Xcel/URS, conversion of OC-normalized PAH concentrations to dwt-normalized concentrations will require a conversion factor much lower than 1% organic carbon. This factor alone will result in an RAO much lower than the 53 µg/g dwt proposed by Xcel/URS.

Protectiveness of a sediment PAH concentration of 5300 µg/g OC

A variety of studies were conducted in support of the Ashland BERA to assess the likely effects of different PAH concentrations in site sediments. The majority of this evidence stems from laboratory exposures of organisms to site sediments. Xcel/URS evaluated these data and proposed a value of 5300 µg PAH/g OC as delineating PAH concentrations with do or don't pose unacceptable risk to benthos. This value seems to be derived through a geometric mean of purported NOEC and LOEC values from a mixture of sediment toxicity studies with *Hyalella azteca*.

There are several aspects of the available data that argue that this value does not have the characteristics of an effect/no effect threshold for benthos. Of the sandy site sediments tested, the sediment with the closest PAH concentration to this proposed RAO is SQT7, with a PAH concentration of 6084 µg total PAH/g OC[2]. This sediment caused >80% mortality of *Hyalella* in a 28-d exposure, and complete mortality of *Lumbriculus variegatus* in a 4-day exposure. Suggesting an RAO that is only 13% lower than a concentration causing egregious toxicity to every benthic organism tested is not consistent with a conceptual goal of little or no toxicity to benthos. URS has suggested that toxicity observed in simultaneous reference sediments reduces confidence in the finding of toxicity to *Hyalella* in SQT7, but the finding of toxicity to *Hyalella* at this PAH concentration is consistent with literature data (discussed further below).

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[2]After the analysis supporting this memo was completed, I was informed by URS that there had been an error in calculating the total PAH values for the SQT samples reported in the URS BERA. Because this error was reported so late, a decision was made to complete this memo using the PAH values previously reported by URS. Although specific values reported in this document would be affected by this error, the overall conclusions would not be greatly affected, hence the decision to proceed based on the values originally reported.

Furthermore, this contention is irrelevant with regard to *Lumbriculus*, to which SQT 7 was highly toxic, as results from the URS bioaccumulation experiment did not indicate that there was extraneous toxicity to *Lumbriculus* in the sandy reference stations.

Equally, or perhaps more significant, is that the Xcel/URS proposed RAO does not provide protection for the midge, *Chironomus dilutus*, for which sediment toxicity data were also available. URS did not succeed in completing toxicity tests on SQT7 or other sediments with midge. However, tests of diluted site sediments conducted by SEH 2001 indicated a EC20 for midge of 4100 µg/g OC. This value is not only lower than the proposed RAO, but was obtained using a dilution series that showed substantially lower toxicity to *Hyalella* than was found by URS in SQT7 and dilutions of SQT1, suggesting that toxicity of those sediments to midge would likely have occurred at even lower concentrations. This suggests strongly that 5310 µg/g OC is not a concentration that would protect against toxicity to *Chironomus dilutus*.

Summary: The site-specific toxicity data, including those collected by Xcel/URS, indicate strongly that an RAO of 5300 µg/g OC would allow for substantial sediment toxicity to all three benthic species tested in this investigation. This does not meet your definition of an appropriately protective value.

Relationship of Site Toxicity Data to Other Information on PAH Toxicity to Benthos

Among other issues, the approach taken by Xcel/URS in the draft BERA was highly empirical and did little to incorporate the larger body of knowledge of PAH effects on benthos. This is a particularly critical issue, because the available data suggest that the threshold for toxicity to benthos likes somewhere in the range of 600 to 6000 µg/g OC, but there are very, very few site-specific data for this concentration range. Thus, it is logical to relate the site specific responses observed in site sediments other information. If there is concordance, then these other sources of information can be used to supplement the site-specific information and, in doing so, provide a stronger basis for deriving an appropriately protective threshold.

Equilibrium partitioning (EqP), as described in the EPA ESB document for PAH mixtures, provides a mechanistic for understanding and predicting the toxicity of PAHs in sediments to benthic organisms. To apply this approach, one must assume or derive an organic carbon partition coefficient (Koc) to describe the distribution of PAH between the solid phase and interstitial water. Because it describes the relative chemical activity of PAHs in the solid phase and interstitial water, Koc is also used to quantify the bioavailability of PAHs in sediments. Although EqP can be applied regardless of the site-specific Koc value, the default approach is to assume that Koc is similar to Kow (log Koc = 0.983*Kow + 0.00028). Because Koc and Kow are nearly equal in value in the default case, it also follows that at steady state, an organism that does not metabolize PAHs will have a body burden (normalized to body lipid) that is roughly equivalent to the OC-normalized PAH concentration in sediment. Thus, the ratio of concentration in organism lipid to concentration in sediment OC (called the Biota Sediment Accumulation Factor or BSAF) is expected to be approximately one if Koc and Kow are similar, thus indicating the default EqP scenario is applicable. This same approach was used in a different context by Xcel/URS in their draft BERA.

The BSAFs for Ashland site sediments can be calculated from the bioaccumulation experiments conducted by URS using *Lumbriculus variegatus*. BSAFs calculated based on total PAH are in the range of 3 to 5 for most stations, indicating that PAH bioavailability in these sediments was, if anything, slightly higher than would be expected if Kow≈Koc. One site, SQT3 showed a much higher BSAF (10) and one site showed a much lower value (0.15). Values much higher than 1 indicate higher than expected bioavailability, which is not inconsistent with the presence of relatively undegraded wood debris, which is common at the site and is consistent with the relatively high OC content of these sediments. A value much lower than 1 indicates a higher Koc value as might result from the presence of large amounts of coal or soot. No values were obtained for SQT1 or SQT7 because these sediments were directly toxic to *Lumbriculus*. However, taken as a whole these BSAF data indicate that the assumption that Kow≈Koc is not unreasonable and is, if anything, perhaps somewhat lenient (i.e., the opposite of environmentally conservative).

The other assumption that is necessary to apply EqP theory to PAH toxicity at the Ashland site is the ratio between the concentration of all PAHs present (hundreds of structures), and those that were actually quantified for the BERA (26 structures). In the EPA ESB document, there is a recommendation that a set of 34 PAHs and PAH homolog series be considered as representing the total PAH concentration for purposes of the ESB. Data relevant to this ratio was collected in the so-called, "forensic study," which included both the 26 structures measured in the URS SQT studies, and the 34 groups in the EPA ESB recommendation. While this should lend itself to a straightforward calculation, there are irregularities in those data that reduce confidence in the calculations. For example, the sum of the two individually-measured methylnaphthalene compounds are significantly greater than the concentration reported for C1-naphthalenes; these concentrations should be equal. As a result, the correction factor for unmeasured PAHs in the BERA has some uncertainty about it which is beyond the scope of this document to fully discuss. For current purposes, a value of 1.2 was chosen, even though higher ratios were observed for other site stations, making this a lenient (as opposed to environmentally conservative) assumption. This was done because SQT1 and SQT7: 1) represent comparatively unweathered material ; 2) appear to be free of woody debris and the uncertainties associated with that material (e.g., retenes); and 3) are the sites whose toxicity was central to the derivation of the RAO based on data for SQT1 and SQT7, the two most toxic samples among the SQT stations, and therefore the samples among the SQT stations that have greatest influence on the RAO. Nonetheless, this value of 1.2 is toward the low end of values reported in the literature for coal tar sites (see Hawthorne et al. 2006) and may be an assumption worthy of further evaluation.

Accepting the assumption that Kow≈Koc, and a total PAH adjustment factor of 1.2, one can use water only toxicity data for PAHs to estimate the concentrations in sediment that would be toxic to *Hyalella azteca* and *Chironomus dilutus*. Schuler et al (2004; ES&T 38:6247) published water only toxicity data for fluoranthene, reporting a water only LC50 for *Hyalella* of 110 μg/l and 59 μg/L for 10-d and 28-d of exposure, respectively, and the 10-d LC50 for *Chironomus dilutus* of 36 μg/L. Assuming a middle-range Koc (5.00) and MW (202) as is represented by fluoranthene, and 1.2 as the adjustment factor for unmeasured PAHs, one would predict that the corresponding LC50's in Ashland sediments would be 10035 μg/g OC for 10-d *Hyalella*, 5383 μg/g OC for 28-d *Hyalella*. These values agree very well with measured responses by Hyalella to SQT1 (10-d LC50 of 12,700 μg/g OC) and SQT7 (28-d mortality of greater than 80% at 6084 μg/g OC), which indicates that the assumptions of the EqP approach are appropriate for these sediments. The calculated 10-d LC50 for midge, 3284 µg/g OC, is a little more than half of the EC50 of 6220 µg/g OC observed in the 10-d sandy sediment dilution study with midge (SEH 2001), and the 28-d *Hyalella* LC50 from the same study (14400 µg/g OC) was also higher than would be predicted. However, as Xcel/URS has argued consistently, there are some irregularities in the reported organic carbon concentrations from the SEH (2001) studies which may influence this comparison.

Summary: The available data support the applicability of EqP and the EPA ESB assessment approach for predicting the toxicity of PAHs in Ashland site sediments.

Calculation of a Threshold Using the EPA ESB

The EPA ESB document contains procedures for estimating a concentration of PAHs in sediment that would protect roughly 95% of all species[3] from chronic toxicity of PAHs. In the ESB calculation, the overall potency of a PAH mixture depends on the distribution of compounds present. To estimate an ESB for the Ashland site, I calculated a concentration-weighted value based on the PAH composition in SQT7 (from the forensic report) with the rationale that this site was closest to the threshold. The molar concentration of each PAH in the "EMAP34" series of PAHs, and it was multiplied by the chemical specific guideline value from the ESB document. The sum of these products was then divided by the sum of all the molar concentrations to derive an overall ESB of 668 µg/g OC (this was the mean of two replicates, 670.5 and 666.0).

To relate this value to the BERA, one has to further correct for the ratio of the PAHs measured by Xcel/URS to the "EMAP34" on which the ESB is based. As described above, the ratio I have been using is 1.2, which makes the final value 557 µg/g OC, or 2.3 µg/g dwt at 0.415% OC.

Summary: The EPA ESB procedure suggests a value of 557 µg PAH/g OC as protecting roughly 95% of species from chronic toxicity.

Calculation of Thresholds for Benthic Species Tested for Ashland BERA

From the available data, it appears that of the three benthic species used in sediment toxicity tests, the midge *Chironomus dilutus* (formerly *tentans*) is the most sensitive. This is supported by both the comparative toxicity in sediment dilution series tested by SEH (2001) and by the literature data for water-only toxicity of fluoranthene reported by Schuler et al (2004). Therefore, if the goal is to derive an RAO that will protect these three species, then it is the toxicity threshold for midge that will set the threshold.

The first issue is to define what the threshold will be. Statistical significance is sometimes used to define toxicity thresholds, but this can be problematic because it is defined in large part by the concentrations tested and subtleties in data variability, neither of which is relevant to the

[3]The ESB is based on protecting the 95% percentile of species for which there are toxicity data; it is assumed that this is roughly equivalent to 95% of all species.

expected biological effect of exposure. In recent years, greater emphasis has been placed on estimating specific levels of effect using various regression techniques. For this purpose, a 20 percent effect threshold (EC20) is often chosen. While it is difficult to establish whether this is a true "threshold" for adverse effect (i.e., all concentrations below this are "safe"), it becomes difficult to reliably estimate levels of effect lower than this. It also corresponds to a level of effect that is commonly found to be significant in toxicological testing. In selecting the EC20, it is recognized that this does not guarantee the absence of biological effect at this concentration; however, it will be presumed that levels of effect lower than this will be adequately addressed through natural attenuation of residual effects.

Within the toxicity tests conducted for the Ashland BERA, there is only one test that directly determines an EC20 for midge; that was the sandy sediment dilution test by SEH (2001). While this is in some ways to most direct method for estimating this value, this study has been criticized repeatedly by Xcel/URS because of anomalies in the analytical data that make the reported exposure concentrations somewhat uncertain. As a cross check on this value, one can use the larger body of available data, to make estimates of the midge EC20 using responses in other tests and relationships among endpoints. The details of this analysis are described in detail in Attachment A, and are summarized in Table 1 below. Estimates of the midge EC20 range from 1340 to 3930 μg PAH/g OC; converting to a dwt basis assuming a sediment OC of 0.415%, this corresponds 5.57 to 16.3 μg PAH/g dwt. Because of the uncertainties involved, it may be most appropriate to think of the midge EC20 as a range rather than a single value.

Table 1 – Summary of Midge EC20 Estimates

Concentration (μg PAH/g OC)	μg PAH/g dwt. @ 0.415% OC	Summary of Derivation
1340	5.57	Treat SQT7 as *Hyalella* 28-d LC80; adjust from *Hyalella* 28-d LC80 to midge LC20 based on SEH (2001) dilution studies
1770	7.35	Treat SQT7 as *Hyalella* 28-d LC80; adjust from *Hyalella* 28-d LC80 to *Hyalella* 28-d LC50 based on URS (2006) and SEH (2001) dilution studies; adjust to midge LC50 based on Schuler (2004); adjust from midge LC50 to midge LC20 based on SEH (2001) dilution studies.
2020	8.38	Midge LC50 predicted from Schuler (2004); adjustment from LC50 to LC20 based on SEH (2001) dilution study
2560	10.6	*Hyalella* 10-d LC50 from URS (2006) dilution study; adjust from *Hyalella* 10-d LC50 to midge LC50 based on Schuler (2004); adjust midge LC50 to midge LC20 based on SEH (2001) dilution studies.
3930	16.3	Average of LC20 and EC20 from SEH (2001) test with dilutions of contaminated sandy sediment.

Note that these values are still not as low as the calculated EPA ESB concentration of 557 μg PAH/g OC (2.31 μg PAH/g dwt at 0.415% OC). Among the reasons for this is that the EC20 midge is the lowest value from among three species, and would not necessarily protect even more sensitive species. Basing an RAO on the midge EC20 should be done in recognition that effects to highly sensitive organisms are possible, and may require additional attenuation of exposure over time to meet a more stringent definition of "threshold."

Summary: Based on a variety of data sources, the EC20 for midge is expected to lie within a range of 1340 to 3930 μg PAH/g OC. At an OC of 0.415%, this corresponds to 5.6 to 16.3 μg PAH/g dwt.

Coherence of Midge EC20 Range with Aggregate Toxicity Data

Figure 1 shows a summary of all available toxicity data for solid-phase toxicity testing of sandy sediments from the Ashland site (in the absence of UV light), combining data from SEH (1998), SEH (2001), and URS (2006). Also shown are WDNR TEC, MEC, and PEC effect endpoints, the EPA ESB value, and the range of midge EC20 estimates listed in Table 1. As can be seen, the midge EC20 range lies in an area that is consistent with the distribution of toxic and non-toxic samples; that is, most of the toxic samples lie to the right of this range, and most of the non-toxic samples lie to the left. Also obvious is the very limited about of data in the 600 to 6000 μg/g range discussed earlier in the document. Finally, the midge EC20 range is consistent with midrange of the WDNR guidance values.

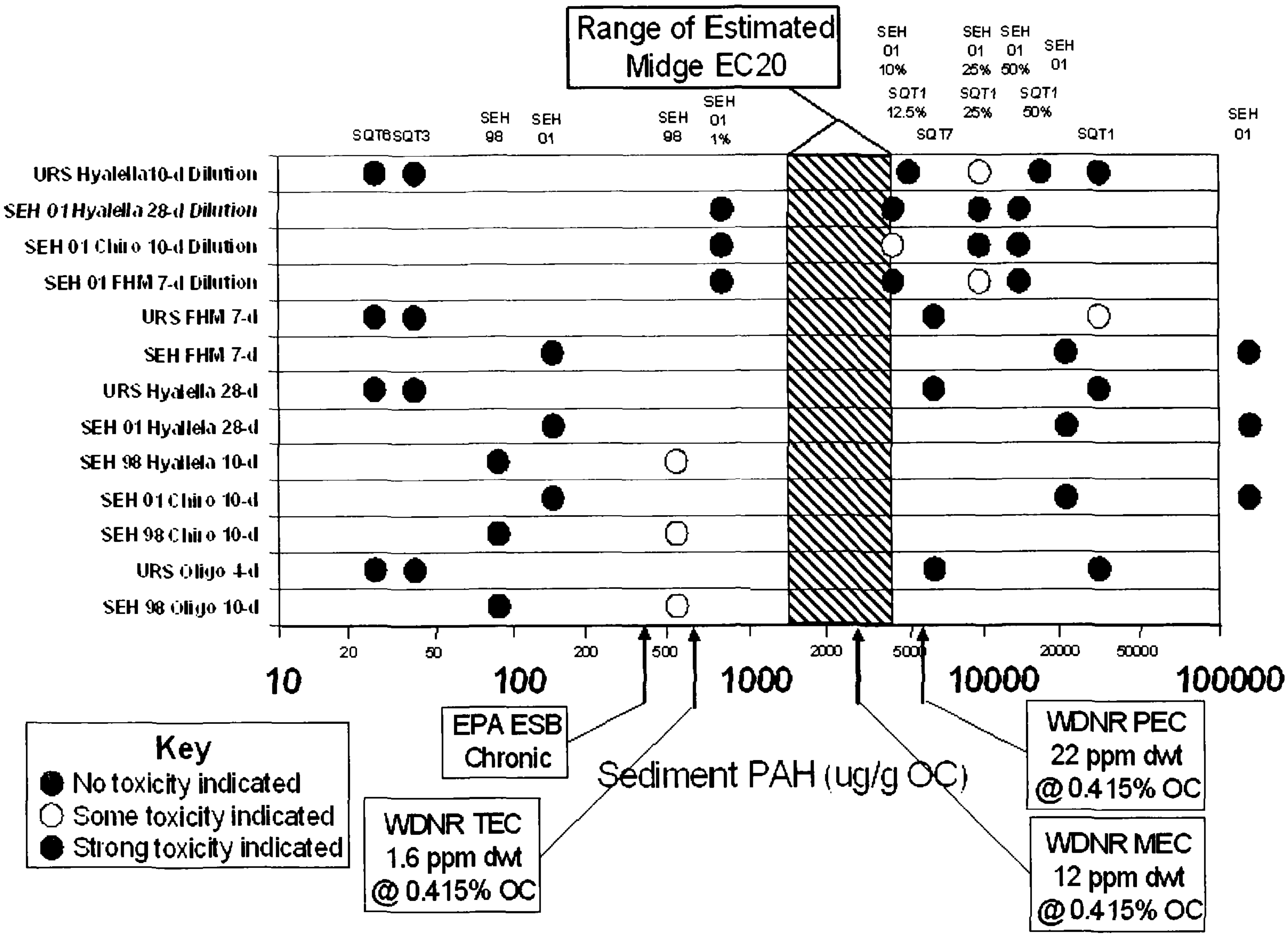
Summary: The range of estimated midge EC20 values is consistent with the distribution of site data and external chemical benchmarks.

Influence of UV Light on PAH Toxicity

The discussion above focuses solely on the effects of site PAHs in the absence of UV. As demonstrated experimentally in studies supporting the BERA, additional toxicity of PAHs can occur when UV light is present. Quantification of these effects, and adjustments to the RAO that may be needed for sediments in shallow water are discussed in a separate memo I forwarded to you previously.

Summary: Effect thresholds discussed in this memo do not include consideration of UV-induced effects, which are discussed in a separate document.

Figure 1 – Summary of Toxicity Data for Sandy Sediments



ATTACHMENT A

ESTIMATION OF MIDGE EC20 VALUES

Because Xcel/URS were unsuccessful at completing toxicity tests with *Chironomus* during the most recent investigations, the only site-specific testing with *Chironomus* across a concentration gradient in sandy sediments was the SEH(2001) dilution study. Regression analysis of these data yielded an EC20 of 4100 μg/g OC. Because of subtle differences in the slopes of the regression line, the estimated LC20 for this study was actually slightly lower, 3760 μg PAH/g OC. Because of this, the mean of these two, 3930 μg PAH/g OC is proposed as the 20% effect level for this study. An uncertainty with this value lies with the analytical characterization which contains some irregularities as pointed out previously by Xcel/URS.

As described in the main body of this document, the water-only fluoranthene data of Schuler et al. (2004) can also be used to estimate sediment effect concentrations. The reported water-only 10-d LC50 for *Chironomus* was 36 μg/L which, give the Kow and molecular weight of fluoranthene, corresponds to a predicted sediment LC50 of 3280 μg PAH/g OC. However, this value needs to be corrected from an LC50 to a 20% effect level. An estimate of this correction is available from the exposure response curve from the SEH(2001) sandy sediment dilution study, in which the ratio of the LC50 to the LC20, which is 6090/3760 or 1.62. Because the LC20 and EC20 were so close in this study, the lethality data were not adjusted downward further for sublethal effects. The results in an estimated LC20 based on the Schuler study of 2020 μg PAH/g OC.

Another point of reference is the toxicity of SQT7 to *Hyalella azteca*; this sediment caused about 80% mortality of *Hyalella* at 6080 μg PAH/g OC. Toxicity testing of this sediment with *Chironomus* was unsuccessful. However, assuming this concentration in this sediment represents an LC80 exposure for *Hyalella*, other data can be used to estimate a response that might be expected from *Chironomus*. One way is to look at the ratio of the *Hyalella* LC80 in the SEH (2001) sandy sediment dilution test to the *Chironomus* effect threshold mentioned above. This would be a ratio of 17800/3930 or 4.53. Dividing the PAH concentration in SQT7 by this value yields 6080/4.53 or 1342 μg PAH/g OC. Another way would be to adjust from a *Hyalella* LC80 to a *Hyallela* LC50 using the ratios of those values from the SEH (1.24) and URS (1.34; geo mean = 1.29), adjust to a *Chironomus* LC50 based on the ratio from Schuler (59/36 = 1.64) and to a *Chironomus* LC20 based on SEH(2001) as above (1.62). This gives an estimated *Chironomus* LC20 of 6080/(1.29*1.64*1.62) = 1770 μg PAH/g OC.

A final method would be to estimate the *Chironomus* LC20 based on the URS(2006) sandy sediment dilution test with *Hyalella*, which gave a 10-d LC50 of 12700 μg PAH/g OC. This can be adjusted to an estimated *Chironomus* 10-d LC50 using the Schuler data (110/36 = 3.06) and to an LC20 based on SEH (2001;1.62). This yields an estimated *Chironomus* 10-d LC20 of 12700/(3.06*1.62) = 2560 μg PAH/g OC.